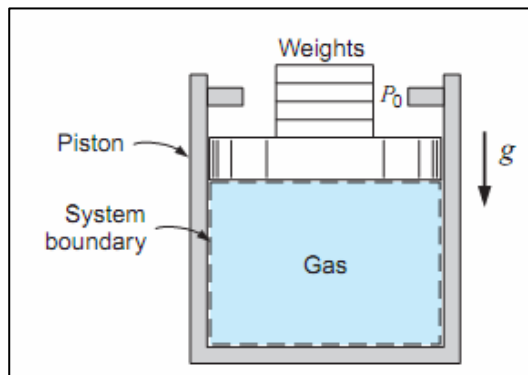


Chapter One

1- A THERMODYNAMIC SYSTEM AND THE CONTROL VOLUME

A thermodynamic system is a device or combination of devices containing a quantity of matter that is being studied. To define this more precisely, a control volume is chosen so that it contains the matter and devices inside a control surface. Everything external to the control volume is the surroundings, with the separation provided by the control surface. The surface may be open or closed to mass flows, and it may have flows of energy in terms of heat transfer and work across it. The boundaries may be movable or stationary. In the case of a control surface that is closed to mass flow, so that no mass can escape or enter the control volume, it is called a control mass containing the same amount of matter at all times. Selecting the gas in the cylinder of Fig.1 as a control volume by placing a control surface around it, we recognize this as a control mass. If a Bunsen burner is placed under the cylinder, the temperature of the gas will increase and the piston will rise. As the piston rises, the boundary of the control mass moves. As we will see later, heat and work cross the boundary of the control mass during this process, but the matter that composes the control mass can always be identified and remains the same.

Fig.1 Example of a control mass.



An isolated system is one that is not influenced in any way by the surroundings. This means that no mass, heat, or work cross the boundary of the system. In many cases, a thermodynamic analysis must be made of a device, such as an air compressor, which has a flow of mass into it, out of it, or both, as shown schematically in Fig. 2. The procedure followed in such an analysis is to specify a control volume that surrounds the device under consideration. The surface of this control volume is the control surface, which may be crossed by mass momentum, as well as heat and work.

Thus the more general control surface defines a control volume, where mass may flow in or out, with a control mass as the special case of no mass flow in or out. Hence the control mass contains a fixed mass at all times, which explains its name. The difference in the formulation of the analysis. The terms closed system (fixed mass) and open system (involving a flow of mass) are sometimes used to make this distinction. Here, we use the term system as a more general and loose description for a mass, device, or

combination of devices that then is more precisely defined when a control volume is selected. The procedure that will be followed in presenting the first and second laws of thermodynamics is first to present these laws for a control mass and then to extend the analysis to the more general control volume.

2- VAPOR–LIQUID–SOLID-PHASE EQUILIBRIUM IN A PURE SUBSTANCE

Consider as a system 1 kg of water contained in the piston/cylinder arrangement shown in Fig. a. Suppose that the piston and weight maintain a pressure of 0.1 MPa in the cylinder and that the initial temperature is 20°C. As heat is transferred to the water, the temperature increases appreciably, the specific volume increases slightly, and the pressure remains constant. When the temperature reaches 99.6°C, additional heat transfer results in a change of phase, as indicated in Fig. 3b. That is, some of the liquid becomes vapor, and during this process both the temperature and pressure remain constant, but the specific volume increases considerably. When the last drop of liquid has vaporized, further transfer of heat results in an increase in both the temperature and specific volume of the vapor, as shown in Fig. 3c. The term saturation temperature designates the temperature at which vaporization takes place at a given pressure. This pressure is called the saturation pressure for the given temperature. Thus, for water at 99.6°C the saturation pressure is 0.1 MPa, and for water at 0.1 MPa the saturation temperature is 99.6°C. For a pure substance there is a definite relation between saturation pressure and saturation temperature.

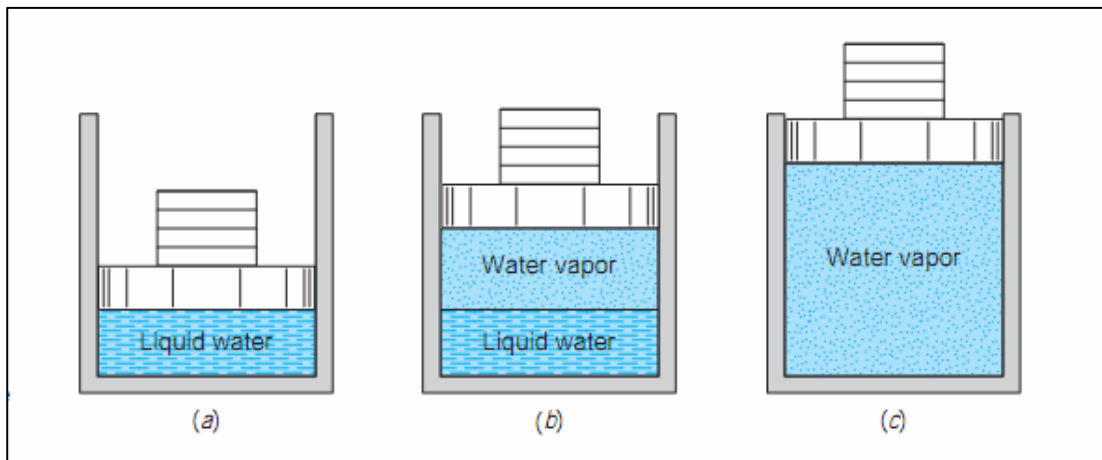


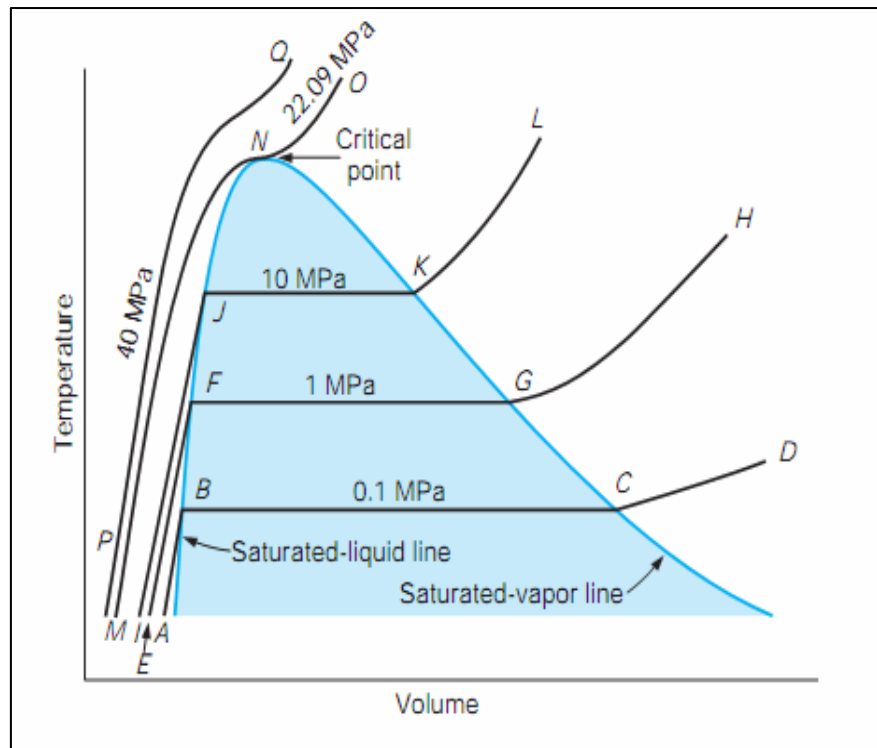
FIGURE 2 Constant-pressure change from liquid to vapor phase for a pure substance.

Consider Fig. 2 again. Let us plot on the temperature–volume diagram of Fig. 3 the constant-pressure line that represents the states through which the water passes as it is heated from the initial state of 0.1 MPa and 20°C. Let state A represent the initial state, B the saturated-liquid state (99.6°C), and line AB the process in which the liquid is heated

from the initial temperature to the saturation temperature. Point C is the saturated-vapor state, and line BC is the constant-temperature process in which the change of phase from liquid to vapor occurs. Line CD represents the process in which the steam is superheated at constant pressure. Temperature and volume both increase during this process. Now let the process take place at a constant pressure of 1 MPa, starting from an initial temperature of 20°C. Point E represents the initial state, in which the specific volume is slightly less than that at 0.1 MPa and 20°C. Vaporization begins at point F, where the temperature is 179.9°C. Point G is the saturated-vapor state, and line GH is the constant-pressure process in which the steam is superheated. In a similar manner, a constant pressure of 10 MPa is represented by line IJKL, for which the saturation temperature is 311.1°C.

At a pressure of 22.09 MPa, represented by line MNO, we find, however, that there is no constant-temperature vaporization process. Instead, point N is a point of inflection with a zero slope. This point is called the critical point. At the critical point the saturated-liquid and saturated-vapor states are identical. The temperature, pressure, and specific volume at the critical point are called the critical temperature, critical pressure, and critical volume.

FIGURE 3
Temperature–volume
diagram for water
showing liquid and vapor
phases



The saturated liquid states in Fig. 4a can be connected by a line called the saturated liquid line, and saturated vapor states in the same figure can be connected by another line, called the saturated vapor line. These two lines meet at the critical point, forming a dome as shown in Fig. 4a and b. All the compressed liquid states are located in the

region to the left of the saturated liquid line, called the compressed liquid region. All the superheated vapor states are located to the right of the saturated vapor line, called the superheated vapor region. In these two regions, the substance exists in a single phase, a liquid or a vapor. All the states that involve both phases in equilibrium are located under the dome, called the saturated liquid–vapor mixture region, or the wet region.

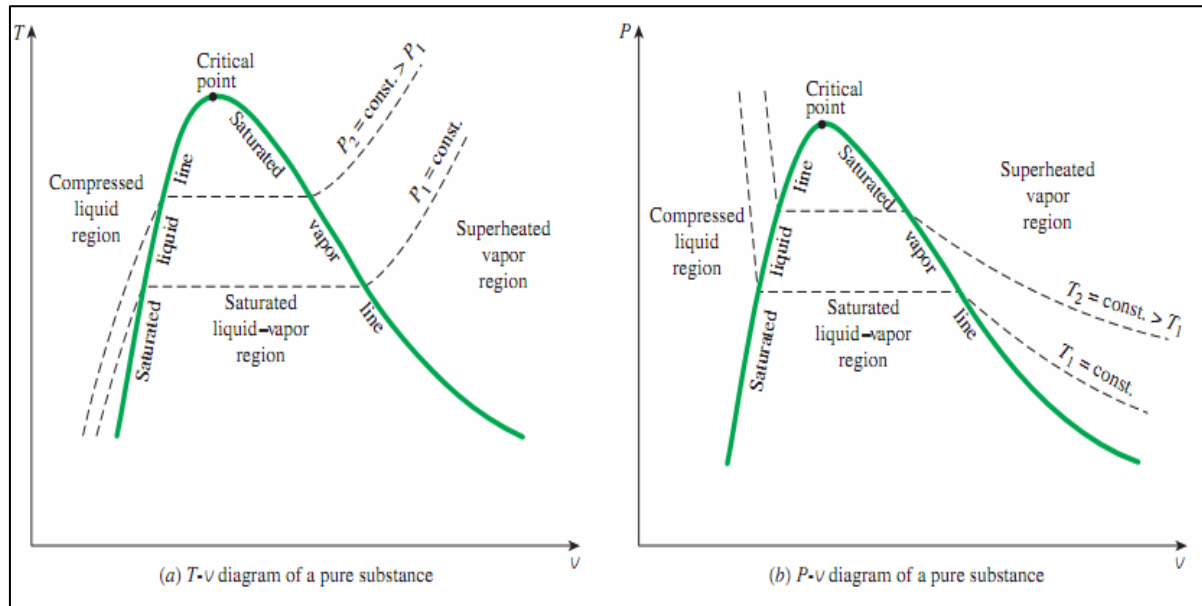


FIGURE 4a and b Property diagrams of a pure substance

<i>Some Critical-Point Data</i>			
	Critical Temperature, °C	Critical Pressure, MPa	Critical Volume, m ³ /kg
Water	374.14	22.09	0.003 155
Carbon dioxide	31.05	7.39	0.002 143
Oxygen	−118.35	5.08	0.002 438
Hydrogen	−239.85	1.30	0.032 192

In Fig. 4, line NJFB represents the saturated-liquid line and line NKGC represents the saturated-vapor line. By convention, the subscript f is used to designate a property of a saturated liquid and the subscript g a property of a saturated vapor (the subscript g being used to denote saturation temperature and pressure). Thus, a saturation condition involving part liquid and part vapor, such as that shown in Fig. 3b, can be shown on T - v coordinates, as in Fig. 5. All of the liquid present is at state f with specific volume v_f and

all of the vapor present is at state g with v_g . The total volume is the sum of the liquid volume and the vapor volume, or

$$V = V_{\text{liq}} + V_{\text{vap}} = m_{\text{liq}} v_f + m_{\text{vap}} v_g$$

The average specific volume of the system v is then

$$v = \frac{V}{m} = \frac{m_{\text{liq}}}{m} v_f + \frac{m_{\text{vap}}}{m} v_g = (1 - x) v_f + x v_g$$

in terms of the definition of quality $x = m_{\text{vap}} / m$.

Using the definition

$$v_{fg} = v_g - v_f$$

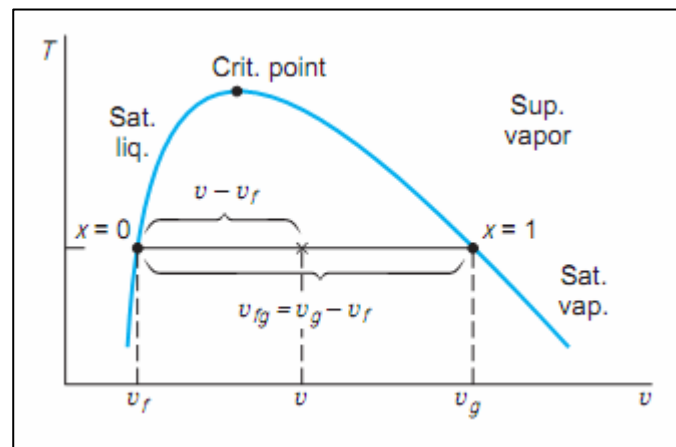
Or

$$v = v_f + x v_{fg}$$

Now the quality x can be viewed as the fraction $(v - v_f) / v_{fg}$ of the distance between saturated liquid and saturated vapor, as indicated in Fig. 5.

And also for h , u , and s .

FIGURE 5 T–v diagram for the two-phase liquid–vapor region showing the quality–specific volume relation.



Through heat transfer, let the temperature increase until it reaches 0.01°C . At this point, however, further heat transfer may cause some of the ice to become vapor and some to become liquid, for at this point it is possible to have the three phases in equilibrium. This point is called the triple point, defined as the state in which all three phases may be present in equilibrium. This whole matter is best summarized by Fig. 6, which shows how the solid, liquid, and vapor phases may exist together in equilibrium.

Along the sublimation line the solid and vapor phases are in equilibrium, along the fusion line the solid and liquid phases are in equilibrium, and along the vaporization line the liquid and vapor phases are in equilibrium. The only point at which all three phases may exist in equilibrium is the triple point. The vaporization line ends at the critical point because there is no distinct change from the liquid phase to the vapor phase above the critical point.

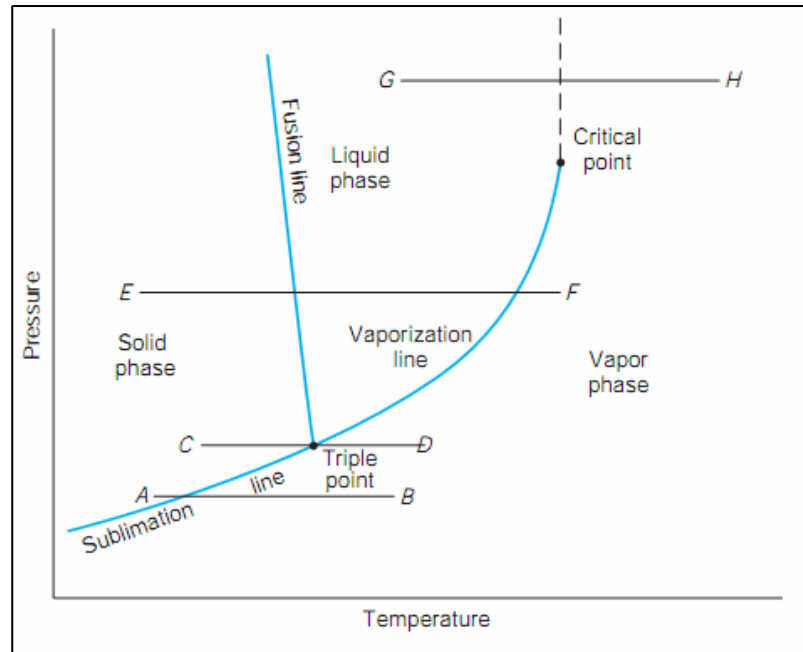


FIGURE 6 P–T diagram for a substance such as water.

Ex1- A mass of 200 g of saturated liquid water is completely vaporized at a constant pressure of 100 kPa. Determine (a) the volume change and (b) the amount of energy transferred to the water?

SOLUTION Saturated liquid water is vaporized at constant pressure. The volume change and the energy transferred are to be determined.

Fig1 . The volume change per unit mass during a vaporization process is v_{fg} , which is the difference between v_g and v_f . Reading these values from Table A–5 at 100 kPa and substituting yield.

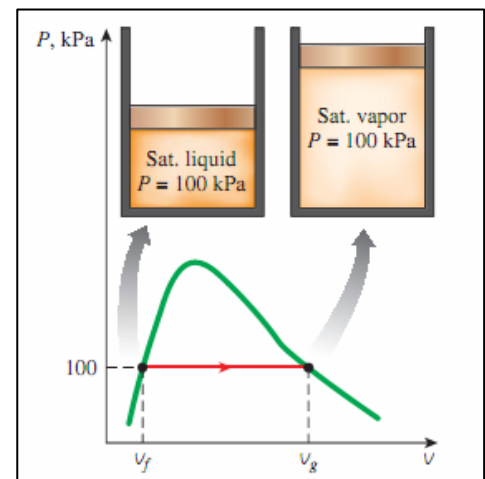
$$v_{fg} = v_g - v_f = 1.6941 - 0.001043 = 1.6931 \text{ m}^3/\text{kg}$$

Thus,

$$\Delta V = m v_{fg} = (0.2 \text{ kg})(1.6931 \text{ m}^3/\text{kg}) = 0.3386 \text{ m}^3$$

(b) The amount of energy needed to vaporize a unit mass of a substance at a given pressure is the enthalpy of vaporization at that pressure, which is $h_{fg} = 2257.5 \text{ kJ/kg}$ for water at 100 kPa. Thus, the amount of energy transferred is

$$m h_{fg} = (0.2 \text{ kg})(2257.5 \text{ kJ/kg}) = 451.5 \text{ kJ}$$



Enthalpy—A Combination Property

The frequently encounter the combination of properties $u + Pv$. For the sake of simplicity and convenience, this combination is defined as a new property, enthalpy, and given the symbol h :

$$h = u + Pv \quad (\text{kJ/kg})$$

or,

$$H = U + PV \quad (\text{kJ})$$

ENERGY TRANSFER BY WORK

Work, like heat, is an energy interaction between a system and its surroundings. As mentioned earlier, energy can cross the boundary of a closed system in the form of heat or work. Therefore, if the energy crossing the boundary of a closed system is not heat, it must be work. Heat is easy to recognize: Its driving force is a temperature difference between the system and its surroundings. Then we can simply say that an energy interaction that is not caused by a temperature difference between a system and its surroundings is work. More specifically, work is the energy transfer associated with a force acting through a distance. A rising piston, a rotating shaft, and an electric wire crossing the system boundaries are all associated with work interactions.

Heat and work are energy transfer mechanisms between a system and its surroundings, and there are many similarities between them:

1. Both are recognized at the boundaries of a system as they cross the boundaries. That is, both heat and work are boundary phenomena.
2. Systems possess energy, but not heat or work.
3. Both are associated with a process, not a state. Unlike properties, heat or work has no meaning at a state.
4. Both are path functions (i.e., their magnitudes depend on the path followed during a process as well as the end states).

Path functions have inexact differentials designated by the symbol d . Therefore, a differential amount of heat or work is represented by dQ or dW , respectively, instead of dQ or dW . Properties, however, are point functions (i.e., they depend on the state only, and not on how a system reaches that state), and they have exact differentials designated by the symbol d . A small change in volume, for example, is represented by dV , and the total volume change during a process between states 1 and 2 is

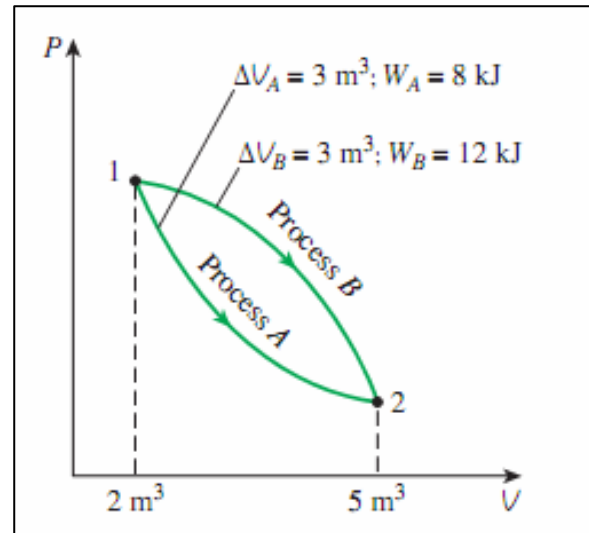
$$\int_1^2 dV = V_2 - V_1 = \Delta V$$

That is, the volume change during process 1–2 is always the volume at state 2 minus the volume at state 1, regardless of the path followed (Fig. 7). The total work done during process 1–2, however, is

$$\int_1^2 \delta W = W_{12} \quad (\text{not } \Delta W)$$

FIGURE 7

Properties are point functions; but heat and work are path functions



WORK DONE AT THE MOVING BOUNDARY OF A SIMPLE COMPRESSIBLE SYSTEM

Consider as a system the gas contained in a cylinder and piston, as in Fig. 8. Remove one of the small weights from the piston, which will cause the piston to move upward a distance dL . We can consider this quasi-equilibrium process and calculate the amount of work W done by the system during this process. The total force on the piston is PA , where P is the pressure of the gas and A is the area of the piston. Therefore, the work δW is

$$\delta W = PA dL$$

But $A dL = dV$, the change in volume of the gas. Therefore,

$$\delta W = P dV$$

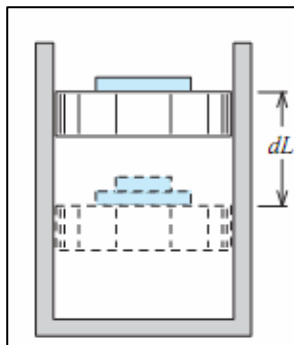


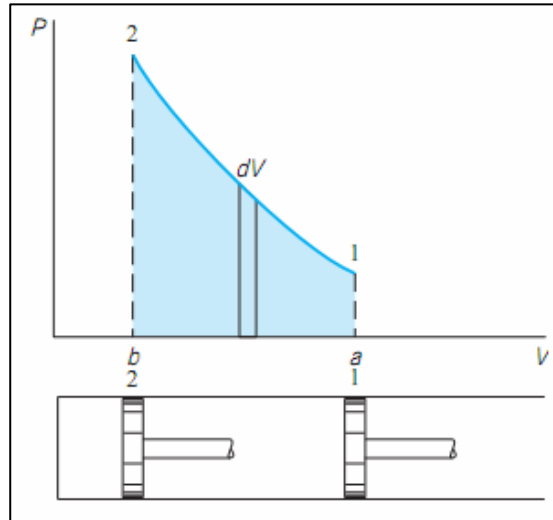
FIGURE 8

Example of work done at the moving boundary of a system in a quasi-equilibrium process.

Let us consider a graphical solution first. We use as an example a compression process

such as occurs during the compression of air in a cylinder, Fig. 9. At the beginning of the process the piston is at position 1, and the pressure is relatively low. This state is represented on a pressure–volume diagram (usually referred to as a P–V diagram).

FIGURE 9 Use of a P–V diagram to show work done at the moving boundary of a system in a quasi-equilibrium process



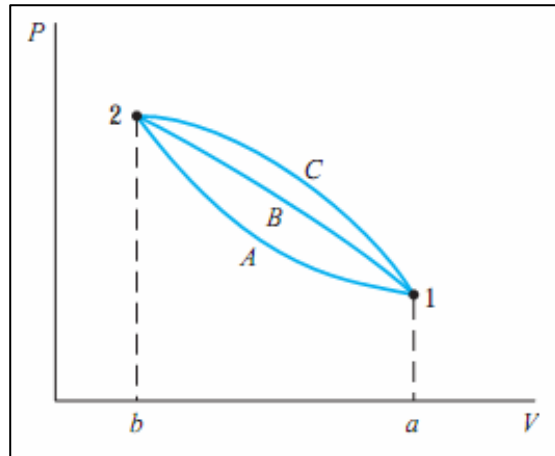
The work done on the air during this compression process can be found by

$${}_1W_2 = \int_1^2 \delta W = \int_1^2 P dV$$

The symbol ${}_1W_2$ is to be interpreted as the work done during the process from state 1 to state 2. It is clear from the P–V diagram that the work done during this process is represented by the area under curve 1–2, area a–1–2–b–a. In this example the volume decreased, and area a–1–2–b–a represents work done on the system. If the process had proceeded from state 2 to state 1 along the same path, the same area would represent work done by the system.

This concept leads to a brief consideration of point and path functions or, to use other terms, exact and inexact differentials. Thermodynamic properties are point functions, a name that comes from the fact that for a given point on a diagram (such as Fig. 10) the state is fixed, and thus there is a definite value for each property corresponding to this point. The differentials of point functions are exact differentials.

FIGURE 10 Various quasi-equilibrium processes between two given states, indicating that work is a path function



It is always keep in mind that we wish to determine the area under the curve in Fig. 10. In connection with this point, we identify the following two classes of problems:

1. The relationship between P and V is given in terms of experimental data or in graphical form (as, for example, the trace on an oscilloscope).
2. The relationship between P and V makes it possible to fit an analytical relationship between them. We may then integrate directly.

Polytropic Process

During actual expansion and compression processes of gases, pressure and volume are often related by $PV^n = C$, where n and C are constants. A process of this kind is called a polytropic process (Fig. 11). Below we develop a general expression for the work done during a polytropic process. The pressure for a polytropic process can be expressed as

$$PV^n = \text{constant}$$

Or

$$P = CV^{-n}$$

throughout the process. The exponent n may be any value from $-\infty$ to $+\infty$, depending on the process. For this type of process, we can integrate as follows:

$$\begin{aligned} PV^n &= \text{constant} = P_1 V_1^n = P_2 V_2^n \\ P &= \frac{\text{constant}}{V^n} = \frac{P_1 V_1^n}{V^n} = \frac{P_2 V_2^n}{V^n} \\ \int_1^2 P dV &= \text{constant} \int_1^2 \frac{dV}{V^n} = \text{constant} \left(\frac{V^{-n+1}}{-n+1} \right) \Big|_1^2 \\ \int_1^2 P dV &= \frac{\text{constant}}{1-n} (V_2^{1-n} - V_1^{1-n}) = \frac{P_2 V_2^n V_2^{1-n} - P_1 V_1^n V_1^{1-n}}{1-n} \\ &= \frac{P_2 V_2 - P_1 V_1}{1-n} \end{aligned}$$

Note that the resulting equation, above, is valid for any exponent n except $n = 1$. Where $n = 1$

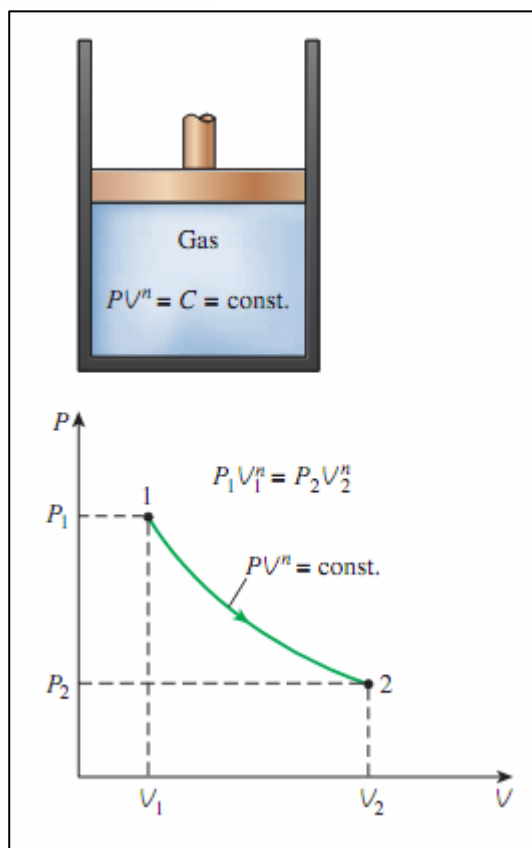
$$PV = \text{constant} = P_1 V_1 = P_2 V_2$$

and

For the special case of $n = 1$ the boundary work becomes

$$W_b = \int_1^2 P dV = \int_1^2 C V^{-1} dV = PV \ln\left(\frac{V_2}{V_1}\right)$$

FIGURE 11
Schematic and P-V diagram for a polytropic process.



THE IDEAL-GAS EQUATION OF STAT

Gas and vapor are often used as synonymous words. The vapor phase of a substance is customarily called a gas when it is above the critical temperature. Vapor usually implies a gas that is not far from a state of condensation.

In 1662, Robert Boyle, an Englishman, observed during his experiments with a vacuum chamber that the pressure of gases is inversely proportional to their volume. In 1802, J. Charles and J. Gay-Lussac, Frenchmen, experimentally determined that at low pressures the volume of a gas is proportional to its temperature. That is,

$$P = R \left(\frac{T}{v} \right)$$

or

$$Pv = RT$$

where the constant of proportionality R is called the gas constant. The equation above is called the ideal-gas equation of state, or simply the ideal-gas relation, and a gas that obeys this relation is called an ideal gas. In this equation, P is the absolute pressure, T is the absolute temperature, and v is the specific volume.

The gas constant R is different for each gas (Fig. 12) and is determined from

$$R = \frac{R_u}{M} \quad (\text{kJ/kg}\cdot\text{K or kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})$$

where R_u is the universal gas constant and M is the molar mass (also called molecular weight) of the gas. The constant R_u is the same for all substances, and its value is

$$R_u = \begin{cases} 8.31447 \text{ kJ/kmol}\cdot\text{K} \\ 8.31447 \text{ kPa}\cdot\text{m}^3/\text{kmol}\cdot\text{K} \\ 0.0831447 \text{ bar}\cdot\text{m}^3/\text{kmol}\cdot\text{K} \\ 1.98588 \text{ Btu/lbmol}\cdot\text{R} \\ 10.7316 \text{ psia}\cdot\text{ft}^3/\text{lbmol}\cdot\text{R} \\ 1545.37 \text{ ft}\cdot\text{lbf/lbmol}\cdot\text{R} \end{cases}$$

FIGURE 12
Different substances have different
gas constants.

Substance	R , kJ/kg·K
Air	0.2870
Helium	2.0769
Argon	0.2081
Nitrogen	0.2968

The mass of a system is equal to the product of its molar mass M and the mole number N :

$$m = MN \quad (\text{kg})$$

The values of R and M for several substances are given in Table A–1. The ideal-gas equation of state can be written in several different forms:

$$\begin{aligned} V &= m v \longrightarrow PV = mRT \\ mR &= (MN)R = NR_u \longrightarrow PV = NR_u T \\ V &= N \bar{v} \longrightarrow P\bar{v} = R_u T \end{aligned}$$

For a fixed mass and simplifying, the properties of an ideal gas at two different states are related to each other by

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

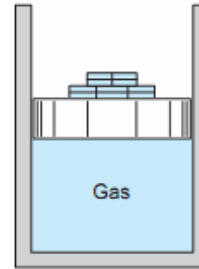
TABLE A-1

Molar mass, gas constant, and critical-point properties

Substance	Formula	Molar mass, <i>M</i> kg/kmol	Gas constant, <i>R</i> kJ/kg·K*	Critical-point properties		
				Temperature, K	Pressure, MPa	Volume, m ³ /kmol
Air	—	28.97	0.2870	132.5	3.77	0.0883
Ammonia	NH ₃	17.03	0.4882	405.5	11.28	0.0724
Argon	Ar	39.948	0.2081	151	4.86	0.0749
Benzene	C ₆ H ₆	78.115	0.1064	562	4.92	0.2603
Bromine	Br ₂	159.808	0.0520	584	10.34	0.1355
<i>n</i> -Butane	C ₄ H ₁₀	58.124	0.1430	425.2	3.80	0.2547
Carbon dioxide	CO ₂	44.01	0.1889	304.2	7.39	0.0943
Carbon monoxide	CO	28.011	0.2968	133	3.50	0.0930
Carbon tetrachloride	CCl ₄	153.82	0.05405	556.4	4.56	0.2759
Chlorine	Cl ₂	70.906	0.1173	417	7.71	0.1242
Chloroform	CHCl ₃	119.38	0.06964	536.6	5.47	0.2403
Dichlorodifluoromethane (R-12)	CCl ₂ F ₂	120.91	0.06876	384.7	4.01	0.2179
Dichlorofluoromethane (R-21)	CHCl ₂ F	102.92	0.08078	451.7	5.17	0.1973
Ethane	C ₂ H ₆	30.070	0.2765	305.5	4.48	0.1480
Ethyl alcohol	C ₂ H ₅ OH	46.07	0.1805	516	6.38	0.1673
Ethylene	C ₂ H ₄	28.054	0.2964	282.4	5.12	0.1242
Helium	He	4.003	2.0769	5.3	0.23	0.0578
<i>n</i> -Hexane	C ₆ H ₁₄	86.179	0.09647	507.9	3.03	0.3677
Hydrogen (normal)	H ₂	2.016	4.1240	33.3	1.30	0.0649
Krypton	Kr	83.80	0.09921	209.4	5.50	0.0924
Methane	CH ₄	16.043	0.5182	191.1	4.64	0.0993
Methyl alcohol	CH ₃ OH	32.042	0.2595	513.2	7.95	0.1180
Methyl chloride	CH ₃ Cl	50.488	0.1647	416.3	6.68	0.1430
Neon	Ne	20.183	0.4119	44.5	2.73	0.0417
Nitrogen	N ₂	28.013	0.2968	126.2	3.39	0.0899
Nitrous oxide	N ₂ O	44.013	0.1889	309.7	7.27	0.0961
Oxygen	O ₂	31.999	0.2598	154.8	5.08	0.0780
Propane	C ₃ H ₈	44.097	0.1885	370	4.26	0.1998
Propylene	C ₃ H ₆	42.081	0.1976	365	4.62	0.1810
Sulfur dioxide	SO ₂	64.063	0.1298	430.7	7.88	0.1217
Tetrafluoroethane (R-134a)	CF ₃ CH ₂ F	102.03	0.08149	374.2	4.059	0.1993
Trichlorofluoromethane (R-11)	CCl ₃ F	137.37	0.06052	471.2	4.38	0.2478
Water	H ₂ O	18.015	0.4615	647.1	22.06	0.0560
Xenon	Xe	131.30	0.06332	289.8	5.88	0.1186

*The unit kJ/kg·K is equivalent to kPa·m³/kg·K. The gas constant is calculated from $R = R_u/M$, where $R_u = 8.31447$ kJ/kmol·K and M is the molar mass.

EX, 2 - Consider as a system the gas in the cylinder shown in Fig.; the cylinder is fitted with a piston on which a number of small weights are placed. The initial pressure is 200 kPa, and the initial volume of the gas is 0.04 m³?



a. Let a Bunsen burner be placed under the cylinder, and let the volume of the gas increase to 0.1 m³ while the pressure remains constant. Calculate the work done by the system during this process.

$${}_1W_2 = \int_1^2 P dV$$

Since the pressure is constant, we conclude from

$${}_1W_2 = P \int_1^2 dV = P(V_2 - V_1)$$

$${}_1W_2 = 200 \text{ kPa} \times (0.1 - 0.04) \text{ m}^3 = 12.0 \text{ kJ}$$

b. Consider the same system and initial conditions, but at the same time that the Bunsen burner is under the cylinder and the piston is rising, remove weights from the piston at such a rate that, during the process, the temperature of the gas remains constant.

$$PV = mRT$$

We note that this is a polytropic process with exponent $n = 1$. From our analysis, we conclude that the work is given by Eq. 4.4 and that the integral in this equation is given by

$$\begin{aligned} {}_1W_2 &= \int_1^2 P dV = P_1 V_1 \ln \frac{V_2}{V_1} \\ &= 200 \text{ kPa} \times 0.04 \text{ m}^3 \times \ln \frac{0.10}{0.04} = 7.33 \text{ kJ} \end{aligned}$$

c. Consider the same system, but during the heat transfer remove the weights at such a rate that the expression $PV^{1.3} = \text{constant}$ describes the relation between pressure and volume during the process. Again, the final volume is 0.1 m³. Calculate the work.

This is a polytropic process in which $n=1.3$.

$$P_2 = 200 \left(\frac{0.04}{0.10} \right)^{1.3} = 60.77 \text{ kPa}$$

$$\begin{aligned} {}_1W_2 &= \int_1^2 P dV = \frac{P_2 V_2 - P_1 V_1}{1 - 1.3} = \frac{60.77 \times 0.1 - 200 \times 0.04}{1 - 1.3} \text{ kPa m}^3 \\ &= 6.41 \text{ kJ} \end{aligned}$$

Chapter Two

THE FIRST LAW OF THERMODYNAMICS

Considered various forms of energy such as heat Q , work W , and total energy E individually, and no attempt is made to relate them to each other during a process. The first law of thermodynamics, also known as the ***conservation of energy principle***, ***provides a sound basis for studying the relationships among the various forms of energy and energy interactions***. Based on experimental observations, the first law of thermodynamics ***states that energy can be neither created nor destroyed during a process; it can only change forms***. Therefore, every bit of energy should be accounted for during a process.

The undergoes a cycle in which it changes from state 1 to state 2 by process A and returns from state 2 to state 1 by process B. This cycle is shown in Fig.1 on a pressure (or other intensive property)–volume (or other extensive property) diagram. From the first law of thermodynamics

$$\oint \delta Q = \oint \delta W$$

Considering the two separate processes, we have

$$\int_1^2 \delta Q_A + \int_2^1 \delta Q_B = \int_1^2 \delta W_A + \int_2^1 \delta W_B$$

Now consider another cycle in which the control mass changes from state 1 to state 2 by process C and returns to state 1 by process B, as before. For this cycle we can write

$$\int_1^2 \delta Q_C + \int_2^1 \delta Q_B = \int_1^2 \delta W_C + \int_2^1 \delta W_B$$

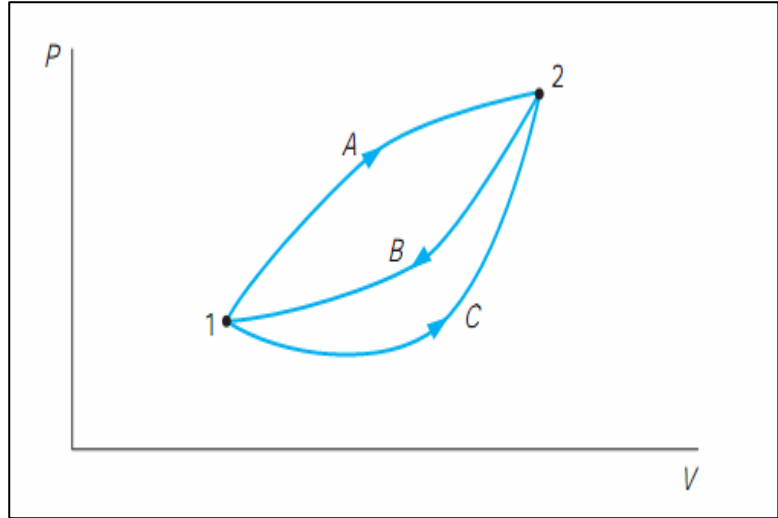
Subtracting the second of these equations from the first, we obtain

$$\int_1^2 \delta Q_A - \int_1^2 \delta Q_C = \int_1^2 \delta W_A - \int_1^2 \delta W_C$$

or, by rearranging,

$$\int_1^2 (\delta Q - \delta W)_A = \int_1^2 (\delta Q - \delta W)_C$$

FIGURE 1
Demonstration of the
existence of
thermodynamic
property E



Since A and C represent arbitrary processes between states 1 and 2, the quantity $\delta Q - \delta W$ is the same for all processes between states 1 and 2. Therefore, $\delta Q - \delta W$ depends only on the initial and final states and not on the path followed between the two states. We conclude that this is a point function, and therefore it is the differential of a property of the mass. This property is the energy of the mass and is given the symbol E. Thus we can write

$$dE = \delta Q - \delta W$$

integrated from an initial state 1 to a final state 2, we have

$$E_2 - E_1 = {}_1Q_2 - {}_1W_2$$

In the study of thermodynamics, it is convenient to consider the bulk kinetic and potential energy separately and then to consider all the other energy of the control mass in a single property that we call the internal energy and to which we give the symbol U. Thus, we would write

$$E = \text{Internal energy} + \text{kinetic energy} + \text{potential energy}$$

or

$$E = U + KE + PE$$

Since the terms comprising E are point functions, we can write

$$dE = dU + d(KE) + d(PE)$$

The first law of thermodynamics for a change of state may therefore be written

$$dE = dU + d(KE) + d(PE) = \delta Q - \delta W$$

This section concludes by deriving an expression for the kinetic and potential energy of a control mass. Consider a mass that is initially at rest relative to the earth, which is taken as the coordinate frame. Let this system be acted on by an external horizontal force F that moves the mass a distance dx in the direction of the force. Thus, there is no change in potential energy. Let there be no heat transfer and no change in internal energy. Then from the first law,

$$\delta W = -F dx = -dKE$$

But

$$F = ma = m \frac{dV}{dt} = m \frac{dx}{dt} \frac{dV}{dx} = mV \frac{dV}{dx}$$

Then

$$dKE = F dx = mV dV$$

Integrating, we obtain

$$\int_{KE=0}^{KE} dKE = \int_{V=0}^V mV dV$$
$$KE = \frac{1}{2} mV^2$$

A similar expression for potential energy can be found. Consider a control mass that is initially at rest and at the elevation of some reference level. Let this mass be acted on by a vertical force F of such magnitude that it raises (in elevation) the mass with constant velocity an amount dZ . Let the acceleration due to gravity at this point be g

$$\delta W = -F dZ = -dPE$$

Then

$$F = ma = mg$$

$$dPE = F dZ = mg dZ$$

Integrating gives

$$\int_{PE_1}^{PE_2} dPE = m \int_{Z_1}^{Z_2} g dZ$$

Assuming that g does not vary with Z (which is a very reasonable assumption for moderate changes in elevation), we obtain

$$PE_2 - PE_1 = mg(Z_2 - Z_1)$$

Now, substituting the expressions for kinetic and potential energy:

$$dE = dU + m\mathbf{V} d\mathbf{V} + mg dZ$$

Integrating for a change of state from state 1 to state 2 with constant g , we get

$$E_2 - E_1 = U_2 - U_1 + \frac{m\mathbf{V}_2^2}{2} - \frac{m\mathbf{V}_1^2}{2} + mgZ_2 - mgZ_1$$

Similarly, substituting these expressions for kinetic and potential energy into we have

$$dE = dU + \frac{d(m\mathbf{V}^2)}{2} + d(mgZ) = \delta Q - \delta W$$

Assuming g is a constant, in the integrated form of this equation,

$$U_2 - U_1 + \frac{m(\mathbf{V}_2^2 - \mathbf{V}_1^2)}{2} + mg(Z_2 - Z_1) = {}_1Q_2 - {}_1W_2$$

EX. 1 A car of mass 1100 kg drives with a velocity such that it has a kinetic energy of 400 kJ (see Fig.). Find the velocity. If the car is raised with a crane, how high should it be lifted in the standard gravitational field to have a potential energy that equals the kinetic energy?

Solution

The standard kinetic energy of the mass is

$$KE = \frac{1}{2}m\mathbf{V}^2 = 400 \text{ kJ}$$

From this we can solve for the velocity:

$$\begin{aligned} \mathbf{V} &= \sqrt{\frac{2 KE}{m}} = \sqrt{\frac{2 \times 400 \text{ kJ}}{1100 \text{ kg}}} \\ &= \sqrt{\frac{800 \times 1000 \text{ N m}}{1100 \text{ kg}}} = \sqrt{\frac{8000 \text{ kg m s}^{-2} \text{ m}}{11 \text{ kg}}} = 27 \text{ m/s} \end{aligned}$$

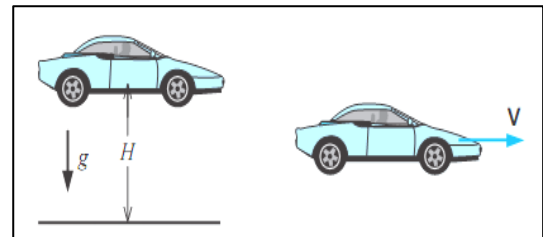
Standard potential energy is

$$PE = mgH$$

so when this is equal to the kinetic energy we get

$$H = \frac{KE}{mg} = \frac{400 \text{ 000 N m}}{1100 \text{ kg} \times 9.807 \text{ m s}^{-2}} = 37.1 \text{ m}$$

Notice the necessity of converting the kJ to J in both calculations.



THE THERMODYNAMIC PROPERTY ENTHALPY

In analyzing specific types of processes, we certain combinations of thermodynamic properties, which are therefore also properties of the substance undergoing the change of state. To demonstrate one such situation, let us consider a control mass undergoing a quasi-equilibrium constant-pressure process, as shown in Fig. 2.

Assume that there are no changes in kinetic or potential energy and that the only work done during the process is that associated with the boundary movement. Taking the gas as our control mass and applying the first law

$${}_1Q_2 = U_2 - U_1 + {}_1W_2$$

The work done can be calculated from the relation

$${}_1W_2 = \int_1^2 P dV$$

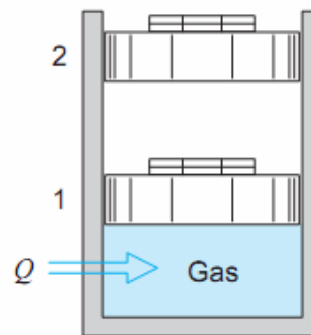
Since the pressure is constant,

$${}_1W_2 = P \int_1^2 dV = P(V_2 - V_1)$$

Therefore,

$$\begin{aligned} {}_1Q_2 &= U_2 - U_1 + P_2 V_2 - P_1 V_1 \\ &= (U_2 + P_2 V_2) - (U_1 + P_1 V_1) \end{aligned}$$

FIGURE 2. The constant-pressure quasi-equilibrium process



The heat transfer during the process is given in terms of the change in the quantity $U + PV$ between the initial and final states. Because all these quantities are thermodynamic properties, that is, functions only of the state of the system, their combination must also have these same characteristics. Therefore, we find it convenient to define a new extensive property, the enthalpy,

$$H \equiv U + PV$$

or, per unit mass,

$$h \equiv u + Pv$$

The heat transfer in a constant-pressure quasi-equilibrium process is equal to the change in enthalpy, which includes both the change in internal energy and the work for this particular process. This is by no means a general result. It is valid for this special case only because the work done during the process is equal to the difference in the PV product for the final and initial states. This would not be true if the pressure had not remained constant during the process.

INTERNAL ENERGY—A THERMODYNAMIC PROPERTY

Internal energy is an extensive property because it depends on the mass of the system. Kinetic and potential energies are also extensive properties. The symbol U designates the internal energy of a given mass of a substance. Following the convention used with other extensive properties, the symbol u designates the internal energy per unit mass. We could speak of u as the specific internal energy, as we do with specific volume. However, because the context will usually make it clear whether u or U is referred to, we will use the term internal energy to refer to both internal energy per unit mass and the total internal energy.

Values for internal energy are found in the steam tables in the same manner as for specific volume. In the liquid–vapor saturation region,

$$U = U_{\text{liq}} + U_{\text{vap}}$$

or

$$mu = m_{\text{liq}}u_f + m_{\text{vap}}u_g$$

Dividing by m and introducing the quality x gives

$$u = (1 - x)u_f + xu_g$$

$$u = u_f + xu_{fg}$$

As an example, the specific internal energy of saturated steam having a pressure of 0.6 MPa and a quality of 95% can be calculated as

$$u = u_f + xu_{fg} = 669.9 + 0.95(1897.5) = 2472.5 \text{ kJ/kg}$$

Values for u in the superheated vapor region are tabulated in Table B.1.3, for compressed liquid in Table B.1.4, and for solid–vapor in Table B.1.5.

Ex1-

Determine the missing property (P , T , or x) and v for water at each of the following states:

- a. $T = 300^\circ\text{C}$, $u = 2780 \text{ kJ/kg}$
- b. $P = 2000 \text{ kPa}$, $u = 2000 \text{ kJ/kg}$

For each case, the two properties given are independent properties and therefore fix the state. For each, we must first determine the phase by comparison of the given information with phase boundary values.

- a. At 300°C , from Table B.1.1, $u_g = 2563.0 \text{ kJ/kg}$. The given $u > u_g$, so the state is in the superheated vapor region at some P less than P_g , which is 8581 kPa . Searching through Table B.1.3 at 300°C , we find that the value $u = 2780$ is between given values of u at 1600 kPa (2781.0) and 1800 kPa (2776.8). Interpolating linearly, we obtain

$$P = 1648 \text{ kPa}$$

Note that quality is undefined in the superheated vapor region. At this pressure, by linear interpolation, we have $v = 0.1542 \text{ m}^3/\text{kg}$.

- b. At $P = 2000 \text{ kPa}$, from Table B.1.2, the given u of 2000 kJ/kg is greater than u_f (906.4) but less than u_g (2600.3). Therefore, this state is in the two-phase region with $T = T_g = 212.4^\circ\text{C}$, and

$$u = 2000 = 906.4 + x1693.8, \quad x = 0.6456$$

Then,

$$v = 0.001177 + 0.6456 \times 0.09845 = 0.06474 \text{ m}^3/\text{kg}.$$

Ex2-

A cylinder fitted with a piston has a volume of 0.1 m^3 and contains 0.5 kg of steam at 0.4 MPa . Heat is transferred to the steam until the temperature is 300°C , while the pressure remains constant.

Determine the heat transfer and the work for this process.

Control mass: Water inside cylinder.

Initial state: P_1 , V_1 , m ; therefore, v_1 is known, state 1 is fixed (at P_1 , v_1 , check steam tables—two-phase region).

Final state: P_2 , T_2 ; therefore, state 2 is fixed (superheated).

Process: Constant pressure.

Diagram: Fig. 5.8.

Model: Steam tables.

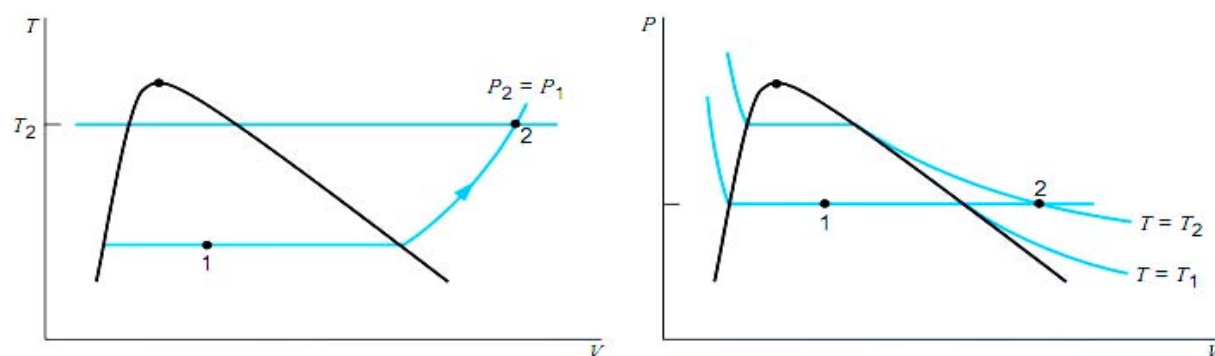
Analysis

There is no change in kinetic energy or potential energy. Work is done by movement at the boundary. Assume the process to be quasi-equilibrium. Since the pressure is constant, we have

$${}_1W_2 = \int_1^2 P dV = P \int_1^2 dV = P(V_2 - V_1) = m(P_2 v_2 - P_1 v_1)$$

Therefore, the first law is, in terms of Q ,

$$\begin{aligned} {}_1Q_2 &= m(u_2 - u_1) + {}_1W_2 \\ &= m(u_2 - u_1) + m(P_2 v_2 - P_1 v_1) = m(h_2 - h_1) \end{aligned}$$



Solution

There is a choice of procedures to follow. State 1 is known, so v_1 and h_1 (or u_1) can be found. State 2 is also known, so v_2 and h_2 (or u_2) can be found. Using the first law and the work equation, we can calculate the heat transfer and work. Using the enthalpies, we have

$$v_1 = \frac{V_1}{m} = \frac{0.1}{0.5} = 0.2 = 0.001\,084 + x_1 0.4614$$

$$x_1 = \frac{0.1989}{0.4614} = 0.4311$$

$$\begin{aligned} h_1 &= h_f + x_1 h_{fg} \\ &= 604.74 + 0.4311 \times 2133.8 = 1524.7 \text{ kJ/kg} \end{aligned}$$

$$h_2 = 3066.8 \text{ kJ/kg}$$

$${}_1Q_2 = 0.5(3066.8 - 1524.7) = 771.1 \text{ kJ}$$

$${}_1W_2 = mP(v_2 - v_1) = 0.5 \times 400(0.6548 - 0.2) = 91.0 \text{ kJ}$$

Therefore,

$$U_2 - U_1 = {}_1Q_2 - {}_1W_2 = 771.1 - 91.0 = 680.1 \text{ kJ}$$

The heat transfer could also have been found from u_1 and u_2 :

$$\begin{aligned} u_1 &= u_f + x_1 u_{fg} \\ &= 604.31 + 0.4311 \times 1949.3 = 1444.7 \text{ kJ/kg} \\ u_2 &= 2804.8 \text{ kJ/kg} \end{aligned}$$

and

$$\begin{aligned} {}_1Q_2 &= U_2 - U_1 + {}_1W_2 \\ &= 0.5(2804.8 - 1444.7) + 91.0 = 771.1 \text{ kJ} \end{aligned}$$

THE CONSTANT-VOLUME AND CONSTANT-PRESSURE SPECIFIC HEATS

Let consider a homogeneous phase of a substance of constant composition. This phase may be a solid, a liquid, or a gas, but no change of phase will occur. We will then define a variable termed the specific heat, the amount of heat required per unit mass to raise the temperature by one degree. Since it would be of interest to examine the relation between the specific heat and other thermodynamic variables

$$\delta Q = dU + \delta W = dU + P dV$$

We find that this expression can be evaluated for two separate special cases:

1. Constant volume, for which the work term ($P dV$) is zero, so that the specific heat (at constant volume) is

$$C_v = \frac{1}{m} \left(\frac{\delta Q}{\delta T} \right)_v = \frac{1}{m} \left(\frac{\partial U}{\partial T} \right)_v = \left(\frac{\partial u}{\partial T} \right)_v$$

2. Constant pressure, for which the work term can be integrated and the resulting PV terms at the initial and final states can be associated with the internal energy terms, thereby leading to the conclusion that the heat transfer can be expressed in terms of the enthalpy change. The corresponding specific heat (at constant pressure) is

$$C_p = \frac{1}{m} \left(\frac{\delta Q}{\delta T} \right)_p = \frac{1}{m} \left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial h}{\partial T} \right)_p$$

As an example, consider the two identical fluid masses shown in Fig. 3. In the first system 100 kJ of heat is transferred to it, and in the second system 100 kJ of work is done on it. Thus, the change of internal energy is the same for each, and therefore the final state and the final temperature are the same in each. Therefore, exactly the same value for the average constant-volume specific heat would be found for this substance for the two processes, even though the two processes are very different as far as heat transfer is concerned.

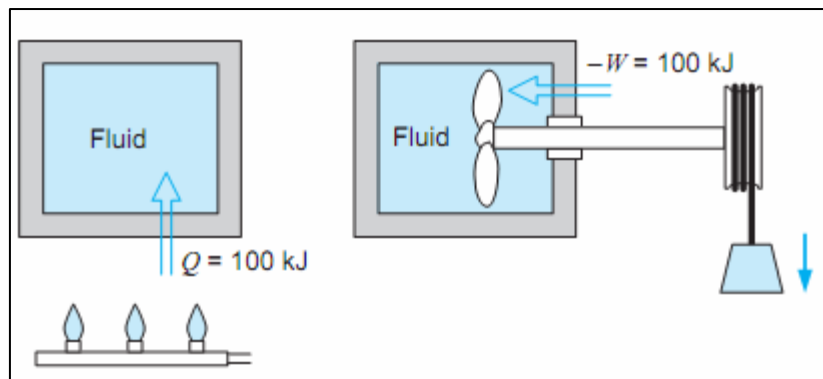


FIGURE 3 Sketch showing two ways in which a given ΔU may be achieved.

Solids and Liquids

As a special case, consider either a solid or a liquid. Since both of these phases are nearly incompressible,

$$dh = du + d(Pv) \approx du + v dP$$

Also, for both of these phases, the specific volume is very small, such that in many cases

$$dh \approx du \approx C dT$$

where C is either the constant-volume or the constant-pressure specific heat, as the two would be nearly the same. In many processes involving a solid or a liquid, we might further assume that the specific heat is constant (unless the process occurs at low temperature or over a wide range of temperatures).

$$h_2 - h_1 \simeq u_2 - u_1 \simeq C(T_2 - T_1)$$

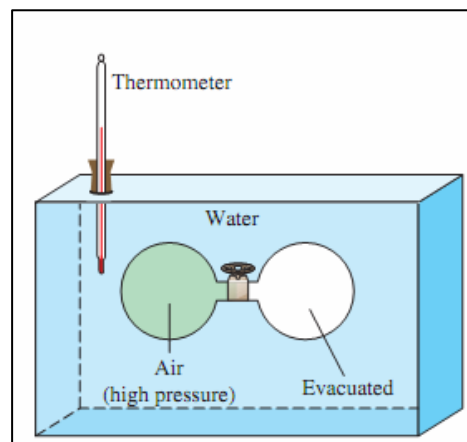
THE INTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEAT OF IDEAL GASES

We defined an ideal gas as a gas whose temperature, pressure, and specific volume are related by $Pv = RT$

For an ideal gas the internal energy is a function of the temperature only. That is,

$$u = u(T)$$

FIGURE 4
Schematic of the experimental apparatus
used by Joule.



In his classical experiment, Joule submerged two tanks connected with a pipe and a valve in a water bath, as shown in Fig. 4. Initially, one tank contained air at a high pressure and the other tank was evacuated.

When thermal equilibrium was attained, he opened the valve to let air pass from one tank to the other until the pressures equalized. Joule observed no change in the temperature of the water bath and assumed that no heat was transferred to or from the air. Since there was also no work done, he concluded that the internal energy of the air did not change even though the volume and the pressure changed. Therefore, he reasoned, the internal energy is a function of temperature only and not a function of pressure or specific volume. (Joule later showed that for gases that deviate significantly from ideal gas behavior, the internal energy is not a function of temperature alone.)

Using the definition of enthalpy and the equation of state of an ideal gas, we have

$$\left. \begin{array}{l} h = u + Pv \\ Pv = RT \end{array} \right\} h = u + RT$$

Since R is constant and $u = u(T)$, it follows that the enthalpy of an ideal gas is also a function of temperature only:

$$h = h(T)$$

Then, the differential changes in the internal energy and enthalpy of an ideal gas can be expressed as

$$du = c_v(T) dT$$

and

$$dh = c_p(T) dT$$

The change in internal energy or enthalpy for an ideal gas during a process from state 1 to state 2 is determined by integrating these equations:

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T) dT \quad (\text{kJ/kg})$$

and

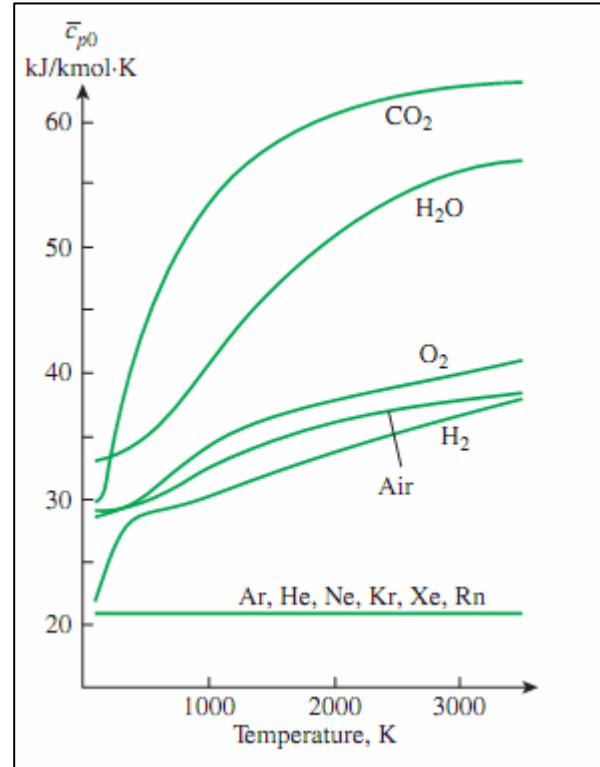
$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T) dT \quad (\text{kJ/kg})$$

To carry out these integrations, we need to have relations for c_v and c_p as functions of temperature.

At low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only. The specific heats of real gases at low pressures are called ideal-gas specific heats, or zero-pressure specific heats, and are often denoted c_{p0} and c_{v0} . Accurate analytical expressions for ideal-gas specific heats, based on direct measurements or calculations from statistical behavior of molecules, are available and are given as third-degree polynomials in the appendix (Table A-2c) for several gases. A plot of $c_{p0}(T)$ data for some common gases is given in Fig. 5.

FIGURE 5

Ideal-gas constant-pressure specific heats for some gases (see Table A–2c for c_p equations)



The specific heats of gases with complex molecules (molecules with two or more atoms) are higher and increase with temperature. Also, the variation of specific heats with temperature is smooth and may be approximated as linear over small temperature intervals (a few hundred degrees or less). Therefore, the specific heat functions can be replaced by the constant average specific heat values. Then, the integrations in these equations can be performed, yielding,

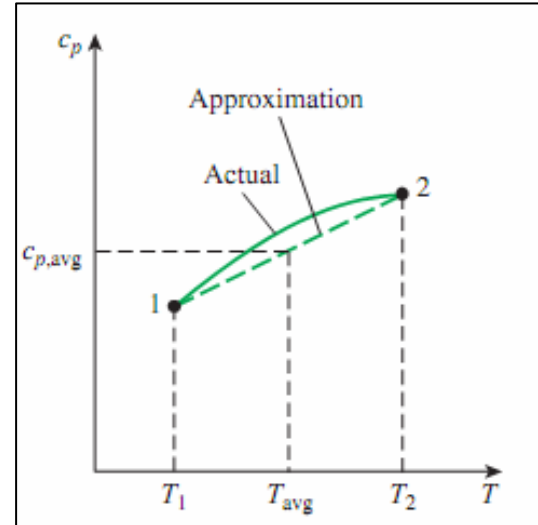
$$u_2 - u_1 = c_{v,avg}(T_2 - T_1) \quad (\text{kJ/kg})$$

and

$$h_2 - h_1 = c_{p,avg}(T_2 - T_1) \quad (\text{kJ/kg})$$

The specific heat values for some common gases are listed as a function of temperature in Table A–2b. The average specific heats $c_{p,avg}$ and $c_{v,avg}$ are evaluated from this table at the average temperature $(T_1 + T_2)/2$, as shown in Fig. 6. If the final temperature T_2 is not known, the specific heats may be evaluated at T_1 or at the anticipated average temperature. Then T_2 can be determined by using these specific heat values. The value of T_2 can be refined, if necessary, by evaluating the specific heats at the new average temperature.

FIGURE 6
For small temperature intervals, the specific heats may be assumed to vary linearly with temperature



Note that the Δu and Δh relations given previously are not restricted to any kind of process. They are valid for all processes. The presence of the constant-volume specific heat c_v in an equation should not lead one to believe that this equation is valid for a constant-volume process only. On the contrary, the relation $\Delta u = c_{v,avg} \Delta T$ is valid for *any* ideal gas undergoing *any* process (Fig. 7). A similar argument can be given for c_p and Δh .

Specific Heat Relations of Ideal Gases

A special relationship between c_p and c_v for ideal gases can be obtained by differentiating the relation $h = u + RT$, which yields

$$dh = du + R dT$$

Replacing dh by $c_p dT$ and du by $c_v dT$ and dividing the resulting expression by dT , we obtain

$$c_p = c_v + R \quad (\text{kJ/kg}\cdot\text{K})$$

This is an important relationship for ideal gases since it enables us to determine c_v from a knowledge of c_p and the gas constant R .

When the specific heats are given on a molar basis, R in the above equation should be replaced by the universal gas constant R_u (Fig. 4–29).

$$\bar{c}_p = \bar{c}_v + R_u \quad (\text{kJ/kmol}\cdot\text{K})$$

At this point, we introduce another ideal-gas property called the **specific heat ratio** k , defined as

$$k = \frac{c_p}{c_v}$$

Ex3- Air at 300 K and 200 kPa is heated at constant pressure to 600 K. Determine the change in internal energy of air per unit mass, using (a) data from the air table (Table A-17), (b) the functional form of the specific heat (Table A-2c), and (c) the average specific heat value (Table A-2b)

SOLUTION The internal energy change of air is to be determined in three different ways.

Assumptions At specified conditions, air can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values.

Analysis The internal energy change Δu of ideal gases depends on the initial and final temperatures only, and not on the type of process. Thus, the following solution is valid for any kind of process.

(a) One way of determining the change in internal energy of air is to read the u values at T_1 and T_2 from Table A-17 and take the difference:

$$u_1 = u @ 300 \text{ K} = 214.07 \text{ kJ/kg}$$

$$u_2 = u @ 600 \text{ K} = 434.78 \text{ kJ/kg}$$

Thus,

$$\Delta u = u_2 - u_1 = (434.78 - 214.07) \text{ kJ/kg} = 220.71 \text{ kJ/kg}$$

(b) The $\bar{c}_p(T)$ of air is given in Table A-2c in the form of a third-degree polynomial expressed as

$$\bar{c}_p(T) = a + bT + cT^2 + dT^3$$

where $a = 28.11$, $b = 0.1967 \times 10^{-2}$, $c = 0.4802 \times 10^{-5}$, and $d = -1.966 \times 10^{-9}$.

$$\bar{c}_v(T) = \bar{c}_p - R_u = (a - R_u) + bT + cT^2 + dT^3$$

$$\Delta \bar{u} = \int_{T_1}^{T_2} \bar{c}_v(T) dT = \int_{T_1}^{T_2} [(a - R_u) + bT + cT^2 + dT^3] dT$$

Performing the integration and substituting the values, we obtain

$$\Delta \bar{u} = 6447 \text{ kJ/kmol}$$

The change in the internal energy on a unit-mass basis is determined by dividing this value by the molar mass of air (Table A-1):

$$\Delta u = \frac{\Delta \bar{u}}{M} = \frac{6447 \text{ kJ/kmol}}{28.97 \text{ kg/kmol}} = 222.5 \text{ kJ/kg}$$

which differs from the tabulated value by 0.8 percent.

(c) The average value of the constant-volume specific heat $c_{v,\text{avg}}$ is determined from Table A-2b at the average temperature of $(T_1 + T_2)/2 = 450 \text{ K}$ to be

$$c_{v,\text{avg}} = c_v @ 450 \text{ K} = 0.733 \text{ kJ/kg}\cdot\text{K}$$

Thus,

$$\begin{aligned} \Delta u &= c_{v,\text{avg}}(T_2 - T_1) = (0.733 \text{ kJ/kg}\cdot\text{K})[(600 - 300)\text{K}] \\ &= 220 \text{ kJ/kg} \end{aligned}$$

THE FIRST LAW AS A RATE EQUATION

The first law as a rate equation that expresses either the instantaneous or average rate at which energy crosses the control surface as heat and work and the rate at which the energy of the control mass changes. In so doing we are departing from a strictly classical point of view, because basically classical thermodynamics deals with systems that are in equilibrium, and time is not a relevant parameter for systems that are in equilibrium.

Consider a time interval δt during which an amount of heat δQ crosses the control surface, an amount of work δW is done by the control mass, the internal energy change is ΔU , the kinetic energy change is ΔKE , and the potential energy change is ΔPE . From the first law we can write

$$\Delta U + \Delta KE + \Delta PE = \delta Q - \delta W$$

Dividing by δt , we have the average rate of energy transfer as heat work and increase of the energy of the control mass:

$$\frac{\Delta U}{\delta t} + \frac{\Delta KE}{\delta t} + \frac{\Delta PE}{\delta t} = \frac{\delta Q}{\delta t} - \frac{\delta W}{\delta t}$$

Taking the limit for each of these quantities as δt approaches zero, we have

$$\lim_{\delta t \rightarrow 0} \frac{\Delta U}{\delta t} = \frac{dU}{dt}, \quad \lim_{\delta t \rightarrow 0} \frac{\Delta(KE)}{\delta t} = \frac{d(KE)}{dt}, \quad \lim_{\delta t \rightarrow 0} \frac{\Delta(PE)}{\delta t} = \frac{d(PE)}{dt}$$

$$\lim_{\delta t \rightarrow 0} \frac{\delta Q}{\delta t} = \dot{Q} \quad (\text{the heat transfer rate})$$

$$\lim_{\delta t \rightarrow 0} \frac{\delta W}{\delta t} = \dot{W} \quad (\text{the power})$$

Therefore, the rate equation form of the first law is

$$\frac{dU}{dt} + \frac{d(KE)}{dt} + \frac{d(PE)}{dt} = \dot{Q} - \dot{W}$$

We could also write this in the form

$$\frac{dE}{dt} = \dot{Q} - \dot{W}$$

It is therefore reasonable to extrapolate this behavior to very low density and to assume that as gas density becomes so low that the ideal-gas model is appropriate, internal energy does not depend on pressure at all but is a function only of temperature. That is, for an ideal gas,

$$Pv = RT \quad \text{and} \quad u = f(T) \text{ only}$$

The relation between the internal energy u and the temperature can be established by using the definition of constant-volume specific heat given by

$$C_v = \left(\frac{\partial u}{\partial T} \right)_v$$

Because the internal energy of an ideal gas is not a function of specific volume, for an ideal gas we can write

$$C_{v0} = \frac{du}{dT}$$
$$du = C_{v0} dT$$

where the subscript 0 denotes the specific heat of an ideal gas. For a given mass m ,

$$dU = mC_{v0} dT$$

From the definition of enthalpy and the equation of state of an ideal gas, it follows that

$$h = u + Pv = u + RT$$

Since R is a constant and u is a function of temperature only, it follows that the enthalpy, h , of an ideal gas is also a function of temperature only. That is,

$$h = f(T)$$

The relation between enthalpy and temperature is found from the constant-pressure specific heat as defined by

$$C_p = \left(\frac{\partial h}{\partial T} \right)_p$$

Since the enthalpy of an ideal gas is a function of the temperature only and is independent of the pressure, it follows that

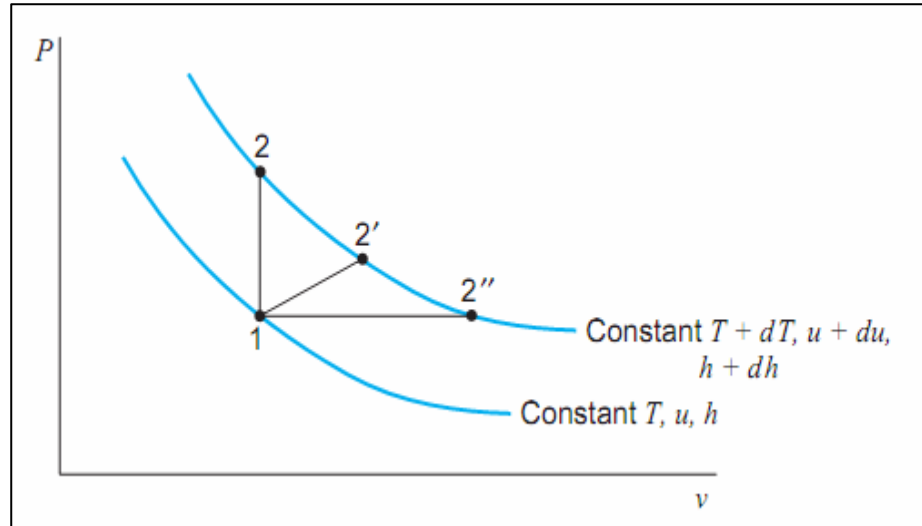
$$C_{p0} = \frac{dh}{dT}$$
$$dh = C_{p0} dT$$

For a given mass m ,

$$dH = mC_{p0} dT$$

The demonstrated in Fig. 7, which shows two lines of constant temperature. Since internal energy and enthalpy are functions of temperature only, these lines of constant temperature are also lines of constant internal energy and constant enthalpy. From state 1 the high temperature can be reached by a variety of paths, and in each case the final state is different. However, regardless of the path, the change in internal energy is the same, as is the change in enthalpy, for lines of constant temperature are also lines of constant u and constant h .

FIGURE 7 P-v diagram for an ideal gas



Because the internal energy and enthalpy of an ideal gas are functions of temperature only, it also follows that the constant-volume and constant-pressure specific heats are also functions of temperature only. That is,

$$C_{v0} = f(T), \quad C_{p0} = f(T)$$

A very important relation between the constant-pressure and constant-volume specific heats of an ideal gas may be developed from the definition of enthalpy:

$$h = u + Pv = u + RT$$

Differentiating and substituting :

$$dh = du + R dT$$

$$C_{p0} dT = C_{v0} dT + R dT$$

Therefore,

$$C_{p0} - C_{v0} = R$$

On a mole basis this equation is written

$$\bar{C}_{p0} - \bar{C}_{v0} = \bar{R}$$

Let us consider the specific heat C_{p0} . There are three possibilities to examine. The situation is simplest if we assume constant specific heat, that is, no temperature dependence. Then it is possible to integrate directly to

$$h_2 - h_1 = C_{p0}(T_2 - T_1)$$

The third possibility is to integrate the results of the calculations of statistical thermodynamics from an arbitrary reference temperature to any other temperature T and to define a function

$$h_T = \int_{T_0}^T C_{p0} dT$$

This function can then be tabulated in a single-entry (temperature) table. Then, between any two states 1 and 2

$$h_2 - h_1 = \int_{T_0}^{T_2} C_{p0} dT - \int_{T_0}^{T_1} C_{p0} dT = h_{T_2} - h_{T_1}$$

Ex3-A piston–cylinder device initially contains air at 150 kPa and 27 C. At this state, the piston is resting on a pair of stops, as shown in Fig., and the enclosed volume is 400 L. The mass of the piston is such that a 350 kPa pressure is required to move it. The air is now heated until its volume has doubled. Determine (a) the final temperature, (b) the work done by the air, and (c) the total heat transferred to the air.

SOLUTION Air in a piston–cylinder device with a set of stops is heated until its volume is doubled. The final temperature, work done, and the total heat transfer are to be determined.

Assumptions **1** Air is an ideal gas since it is at a high temperature and low pressure relative to its critical-point values. **2** The system is stationary and thus the kinetic and potential energy changes are zero, $\Delta KE = \Delta PE = 0$ and $\Delta E = \Delta U$. **3** The volume remains constant until the piston starts moving, and the pressure remains constant afterwards. **4** There are no electrical, shaft, or other forms of work involved.

Analysis We take the contents of the cylinder as the *system*. This is a *closed system* since no mass crosses the system boundary during the process. We observe that a piston-cylinder device typically involves a moving boundary and thus boundary work, W_b . Also, the boundary work is done by the system, and heat is transferred to the system.

(a) The final temperature can be determined easily by using the ideal-gas relation between states 1 and 3 in the following form:

$$\frac{P_1 V_1}{T_1} = \frac{P_3 V_3}{T_3} \longrightarrow \frac{(150 \text{ kPa})(V_1)}{300 \text{ K}} = \frac{(350 \text{ kPa})(2V_1)}{T_3}$$

$$T_3 = 1400 \text{ K}$$

(b) The work done could be determined by integration, but for this case it is much easier to find it from the area under the process curve on a P - V diagram, shown in Fig. 4–32:

$$A = (V_2 - V_1)P_2 = (0.4 \text{ m}^3)(350 \text{ kPa}) = 140 \text{ m}^3 \cdot \text{kPa}$$

Therefore,

$$W_{13} = 140 \text{ kJ}$$

The work is done by the system (to raise the piston and to push the atmospheric air out of the way), and thus it is work output.

(c) Under the stated assumptions and observations, the energy balance on the system between the initial and final states (process 1–3) can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$Q_{\text{in}} - W_{b,\text{out}} = \Delta U = m(u_3 - u_1)$$

The mass of the system can be determined from the ideal-gas relation:

$$m = \frac{P_1 V_1}{RT_1} = \frac{(150 \text{ kPa})(0.4 \text{ m}^3)}{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(300 \text{ K})} = 0.697 \text{ kg}$$

The internal energies are determined from the air table (Table A–17) to be

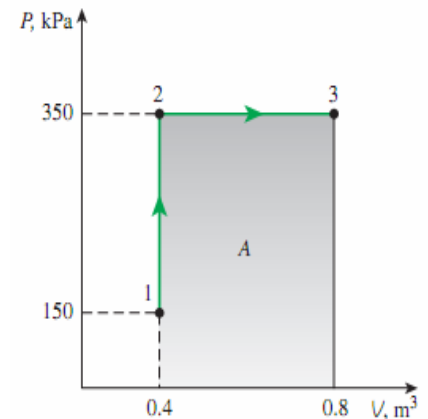
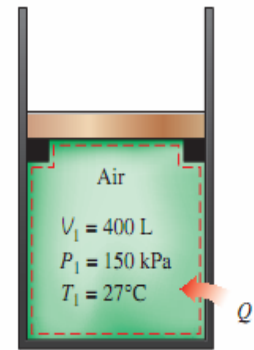
$$u_1 = u_{@ 300 \text{ K}} = 214.07 \text{ kJ/kg}$$

$$u_3 = u_{@ 1400 \text{ K}} = 1113.52 \text{ kJ/kg}$$

Thus,

$$Q_{\text{in}} - 140 \text{ kJ} = (0.697 \text{ kg})[(1113.52 - 214.07) \text{ kJ/kg}]$$

$$Q_{\text{in}} = 767 \text{ kJ}$$



EX4- During the charging of a storage battery, the current i is 20 A and the voltage e is 12.8 V. The rate of heat transfer from the battery is 10 W. At what rate is the internal energy increasing?

Solution

Since changes in kinetic and potential energy are insignificant, the first law can be written as a rate equation in the form of

$$\frac{dU}{dt} = \dot{Q} - \dot{W}$$

$$\dot{W} = \mathcal{E}i = -12.8 \times 20 = -256 \text{ W} = -256 \text{ J/s}$$

Therefore,

$$\frac{dU}{dt} = \dot{Q} - \dot{W} = -10 - (-256) = 246 \text{ J/s}$$

EX 5. A 25-kg cast-iron wood-burning stove, shown in Fig., contains 5 kg of soft pine wood and 1 kg of air. All the masses are at room temperature, 20° C, and pressure, 101 kPa. The wood now burns and heats all the mass uniformly, releasing 1500W. Neglect any air flow and changes in mass of wood and heat losses. Find the rate of change of the temperature(dT/dt) and estimate the time it will take to reach a temperature of 75°C.

Solution

C.V.: The iron, wood and air.
This is a control mass.

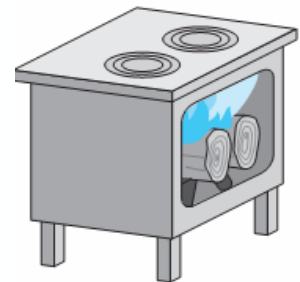
Energy equation rate form: $\dot{E} = \dot{Q} - \dot{W}$

We have no changes in kinetic or potential energy and no change in mass, so

$$\begin{aligned} U &= m_{\text{air}} u_{\text{air}} + m_{\text{wood}} u_{\text{wood}} + m_{\text{iron}} u_{\text{iron}} \\ \dot{E} = \dot{U} &= m_{\text{air}} \dot{u}_{\text{air}} + m_{\text{wood}} \dot{u}_{\text{wood}} + m_{\text{iron}} \dot{u}_{\text{iron}} \\ &= (m_{\text{air}} C_{V\text{air}} + m_{\text{wood}} C_{\text{wood}} + m_{\text{iron}} C_{\text{iron}}) \frac{dT}{dt} \end{aligned}$$

Now the energy equation has zero work, an energy release of \dot{Q} , and becomes

$$\begin{aligned} (m_{\text{air}} C_{V\text{air}} + m_{\text{wood}} C_{\text{wood}} + m_{\text{iron}} C_{\text{iron}}) \frac{dT}{dt} &= \dot{Q} - 0 \\ \frac{dT}{dt} &= \frac{\dot{Q}}{(m_{\text{air}} C_{V\text{air}} + m_{\text{wood}} C_{\text{wood}} + m_{\text{iron}} C_{\text{iron}})} \\ &= \frac{1500}{1 \times 0.717 + 5 \times 1.38 + 25 \times 0.42} \frac{\text{W}}{\text{kg (kJ/kg)}} = 0.0828 \text{ K/s} \end{aligned}$$



Assuming the rate of temperature rise is constant, we can find the elapsed time as

$$\begin{aligned}\Delta T &= \int \frac{dT}{dt} dt = \frac{dT}{dt} \Delta t \\ \Rightarrow \Delta t &= \frac{\Delta T}{\frac{dT}{dt}} = \frac{75 - 20}{0.0828} = 664 \text{ s} = 11 \text{ min}\end{aligned}$$

APPLICATIONS OF STEADY-FLOW ENGINEERING DEVICES

Many engineering devices operate essentially under the same conditions for long periods of time. The components of a steam power plant (turbines, compressors, heat exchangers, and pumps), for example, operate nonstop for months before the system is shut down for maintenance (Fig. 8). Therefore, these devices can be conveniently analyzed as steady-flow devices.

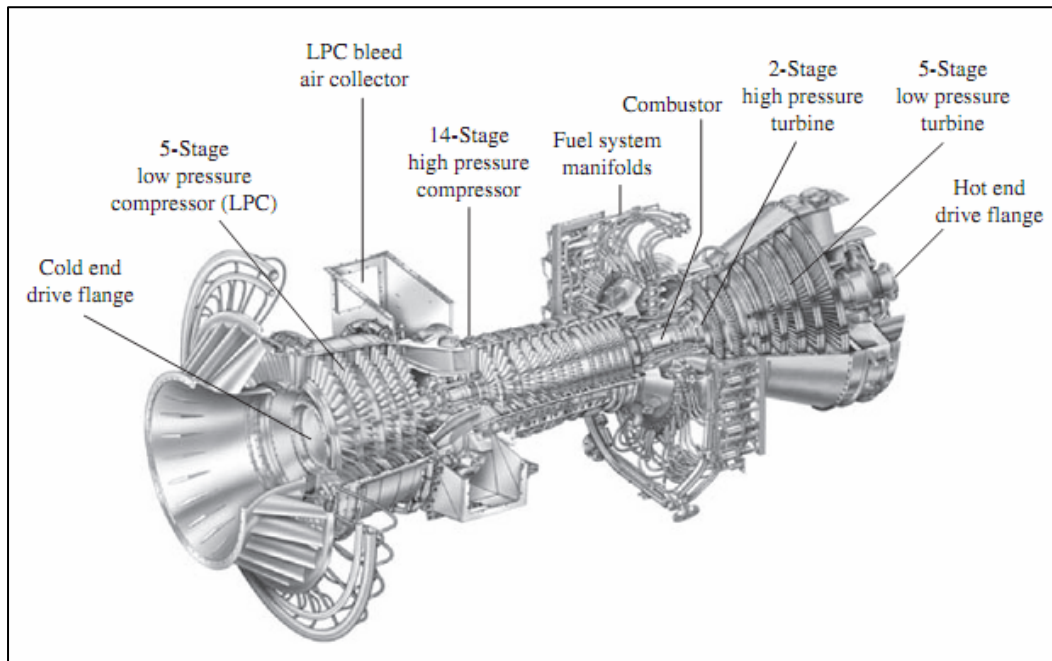


FIGURE 8 A modern land-based gas turbine used for electric power production. This is a General Electric LM5000 turbine. It has a length of 6.2 m, it weighs 12.5 tons, and produces 55.2 MW at 3600 rpm with steam injection.

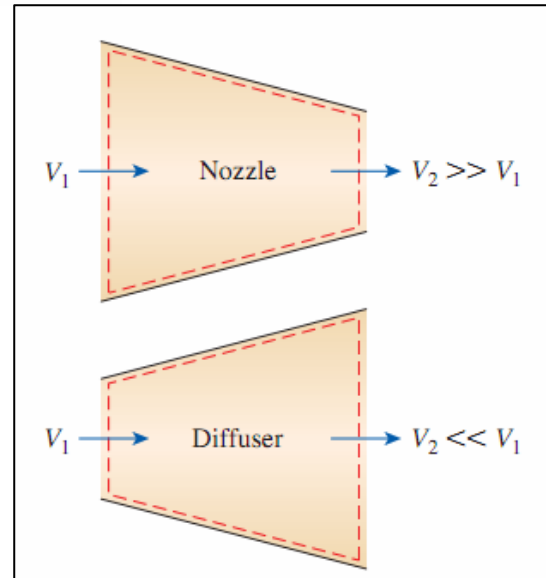
1- Nozzles and Diffusers

Nozzles and diffusers are commonly utilized in jet engines, rockets, spacecraft, and even garden hoses. A nozzle is a device that increases the velocity of a fluid at the expense of pressure. A diffuser is a device that increases the pressure of a fluid by slowing it down. That is, nozzles and diffusers perform opposite tasks. The cross-sectional area of a nozzle decreases in the flow direction for subsonic flows and increases for supersonic flows. The reverse is true for diffusers. The rate of heat transfer between the fluid flowing through a nozzle or a diffuser and the surroundings is usually very small ($\dot{Q} \approx 0$) since the fluid has high velocities, and thus it does not spend enough time in the device for any significant heat transfer to take place. Nozzles and diffusers typically involve no work ($\dot{W} = 0$) and any change in potential energy is negligible ($\Delta p_e \approx 0$). But nozzles and diffusers usually involve very high velocities,

and as a fluid passes through a nozzle or diffuser, it experiences large changes in its velocity (Fig. 9). Therefore, the kinetic energy changes must be accounted for in analyzing the flow through these devices ($\Delta ke \neq 0$).

FIGURE 9

Nozzles and diffusers are shaped so that they cause large changes in fluid velocities and thus kinetic energies



Ex1- Air at 108C and 80 kPa enters the diffuser of a jet engine steadily with a velocity of 200 m/s. The inlet area of the diffuser is 0.4 m². The air leaves the diffuser with a velocity that is very small compared with the inlet velocity. Determine (a) the mass flow rate of the air and (b) the temperature of the air leaving the diffuser.

SOLUTION Air enters the diffuser of a jet engine steadily at a specified velocity. The mass flow rate of air and the temperature at the diffuser exit are to be determined.

Assumptions 1 This is a steady-flow process since there is no change with time at any point and thus $\Delta m_{cv} = 0$ and $\Delta E_{cv} = 0$. 2 Air is an ideal gas since it is at a high temperature and low pressure relative to its critical-point values. 3 The potential energy change is zero, $\Delta pe = 0$. 4 Heat transfer is negligible. 5 Kinetic energy at the diffuser exit is negligible. 6 There are no work interactions.

Analysis We take the *diffuser* as the system (Fig. This is a *control volume* since mass crosses the system boundary during the process. We observe that there is only one inlet and one exit and thus $\dot{m}_1 = \dot{m}_2 = \dot{m}$.

(a) To determine the mass flow rate, we need to find the specific volume of the air first. This is determined from the ideal-gas relation at the inlet conditions:

$$v_1 = \frac{RT_1}{P_1} = \frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(283 \text{ K})}{80 \text{ kPa}} = 1.015 \text{ m}^3/\text{kg}$$

Then,

$$\dot{m} = \frac{1}{v_1} V_1 A_1 = \frac{1}{1.015 \text{ m}^3/\text{kg}} (200 \text{ m/s})(0.4 \text{ m}^2) = \mathbf{78.8 \text{ kg/s}}$$

Since the flow is steady, the mass flow rate through the entire diffuser remains constant at this value.

(b) Under stated assumptions and observations, the energy balance for this steady-flow system can be expressed in the rate form as

$$\underbrace{\dot{E}_{\text{in}} - \dot{E}_{\text{out}}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{\frac{dE_{\text{system}}}{dt}}_{\text{Rate of change in internal, kinetic, potential, etc., energies}} \overset{0 \text{ (steady)}}{=} 0$$

$$\dot{E}_{\text{in}} = \dot{E}_{\text{out}}$$

$$\dot{m} \left(h_1 + \frac{V_1^2}{2} \right) = \dot{m} \left(h_2 + \frac{V_2^2}{2} \right) \quad (\text{since } \dot{Q} \cong 0, \dot{W} = 0, \text{ and } \Delta \text{pe} \cong 0)$$

$$h_2 = h_1 - \frac{V_2^2 - V_1^2}{2}$$

The exit velocity of a diffuser is usually small compared with the inlet velocity ($V_2 \ll V_1$); thus, the kinetic energy at the exit can be neglected. The enthalpy of air at the diffuser inlet is determined from the air table (Table A-17) to be

$$h_1 = h_{@ 283 \text{ K}} = 283.14 \text{ kJ/kg}$$

Substituting, we get

$$\begin{aligned} h_2 &= 283.14 \text{ kJ/kg} - \frac{0 - (200 \text{ m/s})^2}{2} \left(\frac{1 \text{ kJ/kg}}{1000 \text{ m}^2/\text{s}^2} \right) \\ &= 303.14 \text{ kJ/kg} \end{aligned}$$

From Table A-17, the temperature corresponding to this enthalpy value is

$$T_2 = \mathbf{303 \text{ K}}$$



2 - Turbines and Compressors

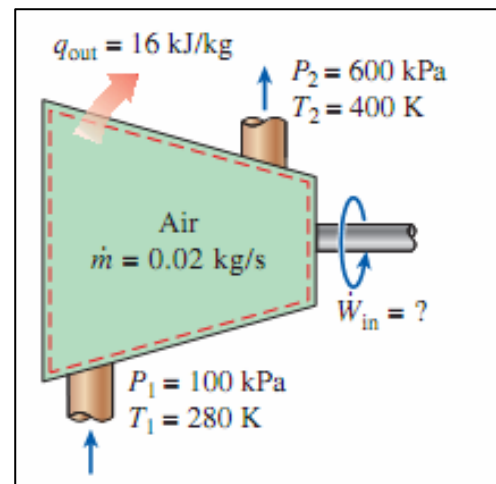
In steam, gas, or hydroelectric power plants, the device that drives the electric generator is the turbine. As the fluid passes through the turbine, work is done against the blades, which are attached to the shaft. Compressors, as well as pumps and fans, are devices used to increase the pressure of a fluid. Work is supplied to these devices from an external source through a rotating shaft. Therefore, compressors involve work inputs. Even though these three devices function similarly, they do differ in the tasks they perform. A fan increases the pressure of a gas slightly and is mainly used to mobilize a gas. A compressor is capable of compressing the gas to very high pressures. Pumps work very much like compressors except that they handle liquids instead of gases.

Note that turbines produce power output whereas compressors, pumps, and fans require power input. Heat transfer from turbines is usually negligible ($\dot{Q} \approx 0$) since they are typically well insulated. Heat transfer is also negligible for compressors unless there is intentional cooling. Potential energy changes are negligible for all of these devices ($\Delta pe \approx 0$). The velocities involved in these devices, with the exception of turbines and fans, are usually too low to cause any significant change in the kinetic energy ($\Delta ke \approx 0$). The fluid velocities encountered in most turbines are very high, and the fluid experiences a significant change in its kinetic energy. However, this change is usually very small relative to the change in enthalpy, and thus it is often disregarded.

Ex.2 Air at 100 kPa and 280 K is compressed steadily to 600 kPa and 400 K. The mass flow rate of the air is 0.02 kg/s, and a heat loss of 16 kJ/kg occurs during the process. Assuming the changes in kinetic and potential energies are negligible, determine the necessary power input to the compressor.

Under stated assumptions and observations, the energy balance for this steady-flow system can be expressed in the rate form as

$$\underbrace{\dot{E}_{in} - \dot{E}_{out}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{\frac{dE_{system}}{dt}}_{\text{Rate of change in internal, kinetic, potential, etc., energies}} \xrightarrow{0 \text{ (steady)}} 0$$



$$\begin{aligned}\dot{E}_{\text{in}} &= \dot{E}_{\text{out}} \\ \dot{W}_{\text{in}} + \dot{m}h_1 &= \dot{Q}_{\text{out}} + \dot{m}h_2 \quad (\text{since } \Delta \text{ke} = \Delta \text{pe} \cong 0) \\ \dot{W}_{\text{in}} &= \dot{m}q_{\text{out}} + \dot{m}(h_2 - h_1)\end{aligned}$$

The enthalpy of an ideal gas depends on temperature only, and the enthalpies of the air at the specified temperatures are determined from the air table (Table A-17) to be

$$\begin{aligned}h_1 &= h_{@ 280 \text{ K}} = 280.13 \text{ kJ/kg} \\ h_2 &= h_{@ 400 \text{ K}} = 400.98 \text{ kJ/kg}\end{aligned}$$

Substituting, the power input to the compressor is determined to be

$$\begin{aligned}\dot{W}_{\text{in}} &= (0.02 \text{ kg/s})(16 \text{ kJ/kg}) + (0.02 \text{ kg/s})(400.98 - 280.13) \text{ kJ/kg} \\ &= \mathbf{2.74 \text{ kW}}\end{aligned}$$

Ex.3 The power output of an adiabatic steam turbine is 5 MW, and the inlet and the exit conditions of the steam are as indicated in Fig.

- Compare the magnitudes of Δh , Δke , and Δpe .
- Determine the work done per unit mass of the steam flowing through the turbine.
- Calculate the mass flow rate of the steam.

Analysis We take the *turbine* as the system. This is a *control volume* since mass crosses the system boundary during the process. We observe that there is only one inlet and one exit and thus $\dot{m}_1 = \dot{m}_2 = \dot{m}$. Also, work is done by the system. The inlet and exit velocities and elevations are given, and thus the kinetic and potential energies are to be considered.

(a) At the inlet, steam is in a superheated vapor state, and its enthalpy is

$$\left. \begin{aligned}P_1 &= 2 \text{ MPa} \\ T_1 &= 400^\circ\text{C}\end{aligned} \right\} h_1 = 3248.4 \text{ kJ/kg} \quad (\text{Table A-6})$$

At the turbine exit, we obviously have a saturated liquid–vapor mixture at 15-kPa pressure. The enthalpy at this state is

$$h_2 = h_f + x_2 h_{fg} = [225.94 + (0.9)(2372.3)] \text{ kJ/kg} = 2361.01 \text{ kJ/kg}$$

Then

$$\Delta h = h_2 - h_1 = (2361.01 - 3248.4) \text{ kJ/kg} = -887.39 \text{ kJ/kg}$$

$$\Delta ke = \frac{V_2^2 - V_1^2}{2} = \frac{(180 \text{ m/s})^2 - (50 \text{ m/s})^2}{2} \left(\frac{1 \text{ kJ/kg}}{1000 \text{ m}^2/\text{s}^2} \right) = 14.95 \text{ kJ/kg}$$

$$\Delta pe = g(z_2 - z_1) = (9.81 \text{ m/s}^2)[(6 - 10) \text{ m}] \left(\frac{1 \text{ kJ/kg}}{1000 \text{ m}^2/\text{s}^2} \right) = -0.04 \text{ kJ/kg}$$

(b) The energy balance for this steady-flow system can be expressed in the rate form as

$$\underbrace{\dot{E}_{in} - \dot{E}_{out}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{\frac{dE_{system}}{dt}}_{\text{Rate of change in internal, kinetic, potential, etc., energies}} \xrightarrow{0 \text{ (steady)}} = 0$$

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{m} \left(h_1 + \frac{V_1^2}{2} + gz_1 \right) = \dot{W}_{out} + \dot{m} \left(h_2 + \frac{V_2^2}{2} + gz_2 \right) \quad (\text{since } \dot{Q} = 0)$$

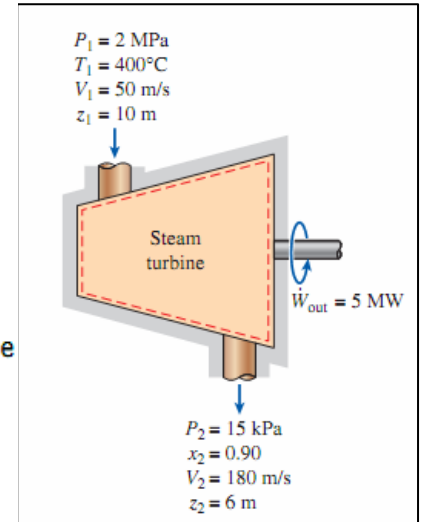
Dividing by the mass flow rate \dot{m} and substituting, the work done by the turbine per unit mass of the steam is determined to be

$$w_{out} = - \left[(h_2 - h_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1) \right] = -(\Delta h + \Delta ke + \Delta pe)$$

$$= -[-887.39 + 14.95 - 0.04] \text{ kJ/kg} = 872.48 \text{ kJ/kg}$$

(c) The required mass flow rate for a 5-MW power output is

$$\dot{m} = \frac{\dot{W}_{out}}{w_{out}} = \frac{5000 \text{ kJ/s}}{872.48 \text{ kJ/kg}} = 5.73 \text{ kg/s}$$



3- Throttling Valves

Throttling valves are any kind of flow-restricting devices that cause a significant pressure drop in the fluid. Some familiar examples are ordinary adjustable valves, capillary tubes, and porous plugs (Fig. 10). Unlike turbines, they produce a pressure drop without involving any work. The pressure drop in the fluid is often accompanied by a large drop in temperature, and for that reason throttling devices are commonly used in refrigeration and air-conditioning applications. The temperature drop (or, sometimes, the temperature rise) during a throttling process is governed by a property called the Joule-Thomson coefficient.

Throttling valves are usually small devices, and the flow through them may be assumed to be adiabatic ($q \cong 0$) since there is neither sufficient time nor large enough area for any effective heat transfer to take place. Also, there is no work done ($w = 0$), and the change in potential energy, if any, is very small ($\Delta pe \cong 0$). Even though the exit velocity is often considerably higher than the inlet velocity, in many cases, the increase in kinetic energy is insignificant ($\Delta ke \cong 0$). Then the conservation of energy equation for this single-stream steady-flow device reduces to

$$h_2 \cong h_1 \quad (\text{kJ/kg})$$

That is, enthalpy values at the inlet and exit of a throttling valve are the same. For this reason, a throttling valve is sometimes called an isenthalpic device.

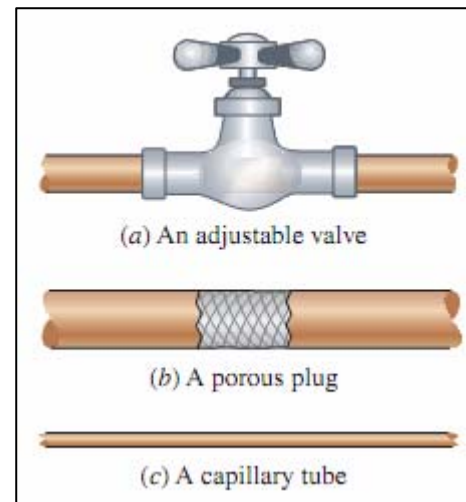
$$u_1 + P_1 v_1 = u_2 + P_2 v_2$$

or

$$\text{Internal energy} + \text{Flow energy} = \text{Constant}$$

FIG.10

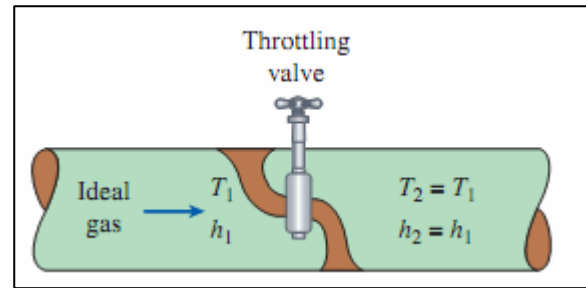
Throttling valves are devices that cause large pressure drops in the fluid



Thus the final outcome of a throttling process depends on which of the two quantities increases during the process. If the flow energy increases during the process ($P_2 v_2 > P_1 v_1$), it can do so at the expense of the internal energy. As a result, internal energy decreases, which is usually accompanied by a drop in temperature. If the product Pv decreases, the internal energy and the temperature of a fluid will increase during a throttling process. In the case of an ideal gas, $h = h(T)$, and thus the temperature has to remain constant during a throttling process (Fig. 11).

FIGURE 11

The temperature of an ideal gas does not change during a throttling ($h = \text{constant}$) process since $h = h(T)$.



Ex4. Refrigerant-134a enters the capillary tube of a refrigerator as saturated liquid at 0.8 MPa and is throttled to a pressure of 0.12 MPa. Determine the quality of the refrigerant at the final state and the temperature drop during this process.

Analysis A capillary tube is a simple flow-restricting device that is commonly used in refrigeration applications to cause a large pressure drop in the refrigerant. Flow through a capillary tube is a throttling process; thus, the enthalpy of the refrigerant remains constant.

$$\text{At inlet: } \left. \begin{array}{l} P_1 = 0.8 \text{ MPa} \\ \text{sat. liquid} \end{array} \right\} \begin{array}{l} T_1 = T_{\text{sat @ } 0.8 \text{ MPa}} = 31.31^\circ\text{C} \\ h_1 = h_f @ 0.8 \text{ MPa} = 95.48 \text{ kJ/kg} \end{array} \quad (\text{Table A-12})$$

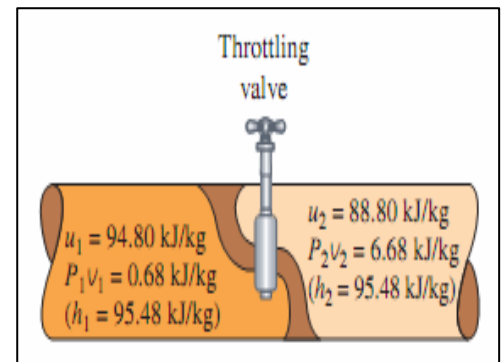
$$\text{At exit: } \begin{array}{l} P_2 = 0.12 \text{ MPa} \\ (h_2 = h_1) \end{array} \longrightarrow \begin{array}{l} h_f = 22.47 \text{ kJ/kg} \\ h_g = 236.99 \text{ kJ/kg} \end{array} \quad T_{\text{sat}} = -22.32^\circ\text{C}$$

Obviously $h_f < h_2 < h_g$; thus, the refrigerant exists as a saturated mixture at the exit state. The quality at this state is

$$x_2 = \frac{h_2 - h_f}{h_{fg}} = \frac{95.48 - 22.47}{236.99 - 22.47} = 0.340$$

Since the exit state is a saturated mixture at 0.12 MPa, the exit temperature must be the saturation temperature at this pressure, which is -22.32°C . Then the temperature change for this process becomes

$$\Delta T = T_2 - T_1 = (-22.32 - 31.31)^\circ\text{C} = -53.63^\circ\text{C}$$



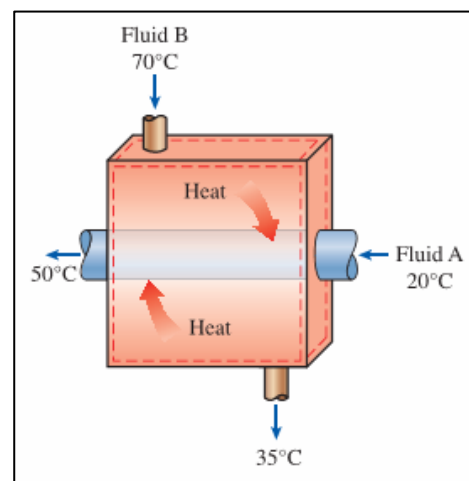
4 Heat Exchangers

As the name implies, heat exchangers are devices where two moving fluid streams exchange heat without mixing. Heat exchangers are widely used in various industries, and they come in various designs. The simplest form of a heat exchanger is a double-tube (also called tube-and-shell) heat exchanger, shown in Fig. 12. It is composed of two concentric pipes of different diameters. One fluid flows in the inner pipe, and the other in the annular space between the two pipes. Heat is transferred from the hot fluid to the cold one through the wall separating them. Sometimes the inner tube makes a couple of turns inside the shell to increase the heat transfer area, and thus the rate of heat transfer. The mixing chambers discussed earlier are sometimes classified as direct-contact heat exchangers. The conservation of mass principle for a heat exchanger in steady operation requires that the sum of the inbound mass flow rates equal the sum of the outbound mass flow rates. This principle can also be expressed as follows: Under steady operation, the mass flow rate of each fluid stream flowing through a heat exchanger remains constant.

Heat exchangers typically involve no work interactions ($w = 0$) and negligible kinetic and potential energy changes ($\Delta ke \cong 0$, $\Delta pe \cong 0$) for each fluid stream. The heat transfer rate associated with heat exchangers depends on how the control volume is selected. Heat exchangers are intended for heat transfer between two fluids *within* the device, and the outer shell is usually well insulated to prevent any heat loss to the surrounding medium.

FIG.12

A heat exchanger can be as simple as two concentric pipes



When the entire heat exchanger is selected as the control volume, Q becomes zero, since the boundary for this case lies just beneath the insulation and little or no heat crosses the boundary (Fig. 13). If, however, only one of the fluids is selected as the

control volume, then heat will cross this boundary as it flows from one fluid to the other and Q will not be zero. In fact, Q in this case will be the rate of heat transfer between the two fluids.

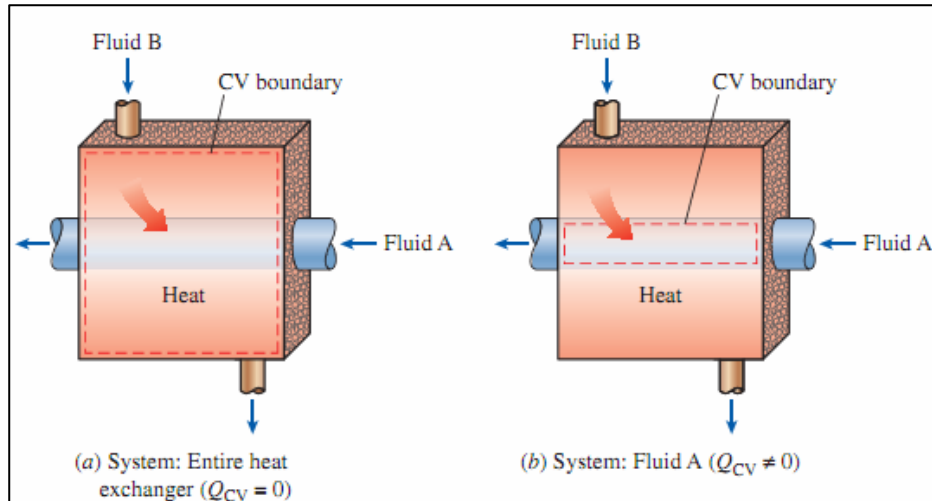
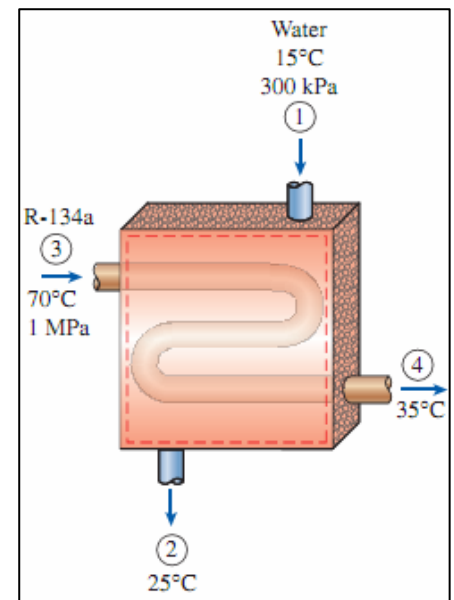


FIG.12 The heat transfer associated with a heat exchanger may be zero or nonzero depending on how the control volume is selected.

Ex.5 Refrigerant-134a is to be cooled by water in a condenser. The refrigerant enters the condenser with a mass flow rate of 6 kg/min at 1 MPa and 70°C and leaves at 35°C. The cooling water enters at 300 kPa and 15°C and leaves at 25°C. Neglecting any pressure drops, determine (a) the mass flow rate of the cooling water required and (b) the heat transfer rate from the refrigerant to water.



(a) Under the stated assumptions and observations, the mass and energy balances for this steady-flow system can be expressed in the rate form as follows:

Mass balance: $\dot{m}_{in} = \dot{m}_{out}$

for each fluid stream since there is no mixing. Thus,

$$\dot{m}_1 = \dot{m}_2 = \dot{m}_w$$

$$\dot{m}_3 = \dot{m}_4 = \dot{m}_R$$

Energy balance:

$$\underbrace{\dot{E}_{in} - \dot{E}_{out}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{\frac{dE_{system}}{dt}}_{\text{Rate of change in internal, kinetic, potential, etc., energies}} \overset{0 \text{ (steady)}}{=} 0$$

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{m}_1 h_1 + \dot{m}_3 h_3 = \dot{m}_2 h_2 + \dot{m}_4 h_4 \quad (\text{since } \dot{Q} \cong 0, \dot{W} = 0, ke \cong pe \cong 0)$$

Combining the mass and energy balances and rearranging give

$$\dot{m}_w(h_1 - h_2) = \dot{m}_R(h_4 - h_3)$$

Now we need to determine the enthalpies at all four states. Water exists as a compressed liquid at both the inlet and the exit since the temperatures at both locations are below the saturation temperature of water at 300 kPa (133.52°C). Approximating the compressed liquid as a saturated liquid at the given temperatures, we have

$$h_1 \cong h_{f@15^\circ\text{C}} = 62.982 \text{ kJ/kg} \quad (\text{Table A-4})$$

$$h_2 \cong h_{f@25^\circ\text{C}} = 104.83 \text{ kJ/kg}$$

The refrigerant enters the condenser as a superheated vapor and leaves as a compressed liquid at 35°C. From refrigerant-134a tables,

$$\left. \begin{array}{l} P_3 = 1 \text{ MPa} \\ T_3 = 70^\circ\text{C} \end{array} \right\} h_3 = 303.87 \text{ kJ/kg} \quad (\text{Table A-13})$$

$$\left. \begin{array}{l} P_4 = 1 \text{ MPa} \\ T_4 = 35^\circ\text{C} \end{array} \right\} h_4 \cong h_{f@35^\circ\text{C}} = 100.88 \text{ kJ/kg} \quad (\text{Table A-11})$$

Substituting, we find

$$\begin{aligned} \dot{m}_w(62.982 - 104.83) \text{ kJ/kg} &= (6 \text{ kg/min})[(100.88 - 303.87) \text{ kJ/kg}] \\ \dot{m}_w &= \mathbf{29.1 \text{ kg/min}} \end{aligned}$$

(b) To determine the heat transfer from the refrigerant to the water, we have to choose a control volume whose boundary lies on the path of heat transfer. We can choose the volume occupied by either fluid as our control volume. For no particular reason, we choose the volume occupied by the water. All the assumptions stated earlier apply, except that the heat transfer is no longer zero. Then assuming heat to be transferred to water, the energy balance for this single-stream steady-flow system reduces to

$$\underbrace{\dot{E}_{\text{in}} - \dot{E}_{\text{out}}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{\frac{dE_{\text{system}}}{dt}}_{\text{Rate of change in internal, kinetic, potential, etc., energies}} \overset{0 \text{ (steady)}}{=} 0$$

$$\dot{E}_{\text{in}} = \dot{E}_{\text{out}}$$

$$\dot{Q}_{w, \text{in}} + \dot{m}_w h_1 = \dot{m}_w h_2$$

Rearranging and substituting,

$$\begin{aligned} \dot{Q}_{w, \text{in}} &= \dot{m}_w (h_2 - h_1) = (29.1 \text{ kg/min})[(104.83 - 62.982) \text{ kJ/kg}] \\ &= \mathbf{1218 \text{ kJ/min}} \end{aligned}$$

5 Pipe and Duct Flow

The transport of liquids or gases in pipes and ducts is of great importance in many engineering applications. Flow through a pipe or a duct usually satisfies the steady-flow conditions and thus can be analyzed as a steady-flow process. This, of course, excludes the transient start-up and shut-down periods. The control volume can be selected to coincide with the interior surfaces of the portion of the pipe or the duct that we are interested in analyzing. Under normal operating conditions, the amount of heat gained or lost by the fluid may be very significant, particularly if the pipe or duct is long (Fig.13). If the control volume involves a heating section (electric wires), a fan, or a pump (shaft), the work interactions should be considered (Fig. 14). Of these, fan work is usually small and often neglected in energy analysis.

FIG.13

Heat losses from a hot fluid flowing through an uninsulated pipe or duct to the cooler environment may be very significant

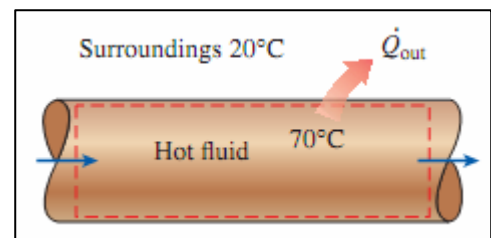
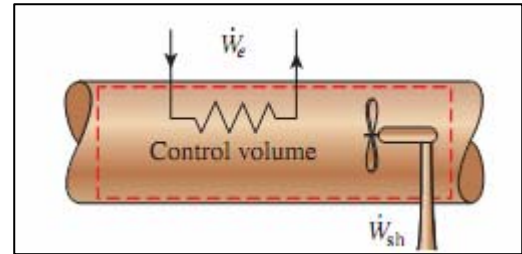


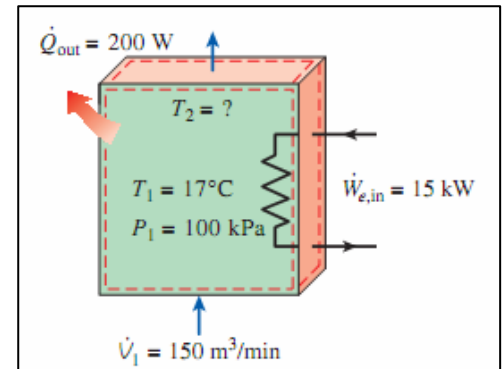
FIG.14

Pipe or duct flow may involve more than one form of work at the same time



Ex.6 The electric heating systems used in many houses consist of a simple duct with resistance heaters. Air is heated as it flows over resistance wires. Consider a 15-kW electric heating system. Air enters the heating section at 100 kPa and 17°C with a volume flow rate of 150 m³/min. If heat is lost from the air in the duct to the surroundings at a rate of 200 W, determine the exit temperature of air

$$\underbrace{\dot{E}_{in} - \dot{E}_{out}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{\frac{dE_{system}}{dt}}_{\text{Rate of change in internal, kinetic, potential, etc., energies}} \xrightarrow{0 \text{ (steady)}} = 0$$



$$\begin{aligned}\dot{E}_{in} &= \dot{E}_{out} \\ \dot{W}_{e,in} + \dot{m}h_1 &= \dot{Q}_{out} + \dot{m}h_2 \quad (\text{since } \Delta ke \cong \Delta pe \cong 0) \\ \dot{W}_{e,in} - \dot{Q}_{out} &= \dot{m}c_p(T_2 - T_1)\end{aligned}$$

From the ideal-gas relation, the specific volume of air at the inlet of the duct is

$$v_1 = \frac{RT_1}{P_1} = \frac{(0.287 \text{ kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})(290 \text{ K})}{100 \text{ kPa}} = 0.832 \text{ m}^3/\text{kg}$$

The mass flow rate of the air through the duct is determined from

$$\dot{m} = \frac{\dot{V}_1}{v_1} = \frac{150 \text{ m}^3/\text{min}}{0.832 \text{ m}^3/\text{kg}} \left(\frac{1 \text{ min}}{60 \text{ s}} \right) = 3.0 \text{ kg/s}$$

Substituting the known quantities, the exit temperature of the air is determined to be

$$\begin{aligned}(15 \text{ kJ/s}) - (0.2 \text{ kJ/s}) &= (3 \text{ kg/s})(1.005 \text{ kJ/kg}\cdot^\circ\text{C})(T_2 - 17^\circ\text{C}) \\ T_2 &= \mathbf{21.9^\circ\text{C}}\end{aligned}$$

Chapter Two

THE SECOND LAW OF THERMODYNAMICS

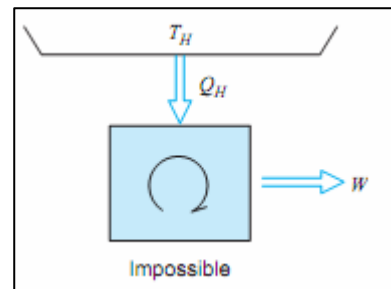
The first law of thermodynamics states that during any cycle that a system undergoes, the cyclic integral of the heat is equal to the cyclic integral of the work. The first law, however, places no restrictions on the direction of flow of heat and work. A cycle in which a given amount of heat is transferred from the system and an equal amount of work is done on the system satisfies the first law just as well as a cycle in which the flows of heat and work are reversed. However, we know from our experience that a proposed cycle that does not violate the first law does not ensure that the cycle will actually occur. It is this kind of experimental evidence that led to the formulation of the second law of thermodynamics.

THE SECOND LAW OF THERMODYNAMICS

On the basis of the matter considered in the previous section, we are now ready to state the second law of thermodynamics. There are two classical statements of the second law, known as the Kelvin–Planck statement and the Clausius statement.

The Kelvin–Planck statement: *It is impossible to construct a device that will operate in a cycle and produce no effect other than the raising of a weight and the exchange of heat with a single reservoir.* See Fig. 1.

FIG.1 The
Kelvin–Planck statement



This statement ties in with our discussion of the heat engine. In effect, it states that it is impossible to construct a heat engine that operates in a cycle, receives a given amount of heat from a high-temperature body, and does an equal amount of work. The only alternative is that some heat must be transferred from the working fluid at a lower temperature to a low-temperature body. Thus, work can be done by the transfer of heat only if there are two temperature levels, and heat is transferred from the high-temperature body to the heat engine and also from the heat engine to the low-temperature body. This implies that it is impossible to build a heat engine that has a thermal efficiency of 100%.

The Clausius statement: *It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.* See Fig. 2.

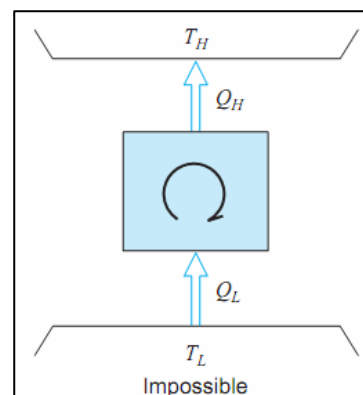
This statement is related to the refrigerator or heat pump. In effect, it states that it is impossible to construct a refrigerator that operates without an input of work. This also implies that the COP is always less than infinity.

Three observations should be made about these two statements. The first observation is that both are negative statements. It is, of course, impossible to prove these negative statements. However, we can say that the second law of thermodynamics (like every other law of nature) rests on experimental evidence. Every relevant experiment that has been conducted, either directly or indirectly, verifies the second law, and no experiment has ever been conducted that contradicts the second law. The basis of the second law is therefore experimental evidence.

A second observation is that these two statements of the second law are equivalent.

Two statements are equivalent if the truth of either statement implies the truth of the other or if the violation of either statement implies the violation of the other. That a violation of the Clausius statement implies a violation of the Kelvin–Planck statement may be shown. The device at the left in Fig. 3 is a refrigerator that requires no work and thus violates the Clausius statement. Let an amount of heat Q_L be transferred from the low-temperature reservoir to this refrigerator, and let the same amount of heat Q_L be transferred to the high-temperature reservoir. Let an amount of heat Q_H that is greater than Q_L be transferred from the high-temperature reservoir to the heat engine, and let the engine reject the amount of heat Q_L as it does an amount of work, W , that equals $Q_H - Q_L$. Because there is no net heat transfer to the low-temperature reservoir, the low-temperature reservoir, along with the heat engine and the refrigerator, can be considered together as a device that operates in a cycle and produces no effect other than the raising of a weight (work) and the exchange of heat with a single reservoir. Thus, a violation of the Clausius statement implies a violation of the Kelvin–Planck statement. The complete equivalence of these two statements is established when it is also shown that a violation of the Kelvin–Planck statement implies a violation of the Clausius statement. This is left as an exercise for the student.

FIG.2 The
Clausius statement



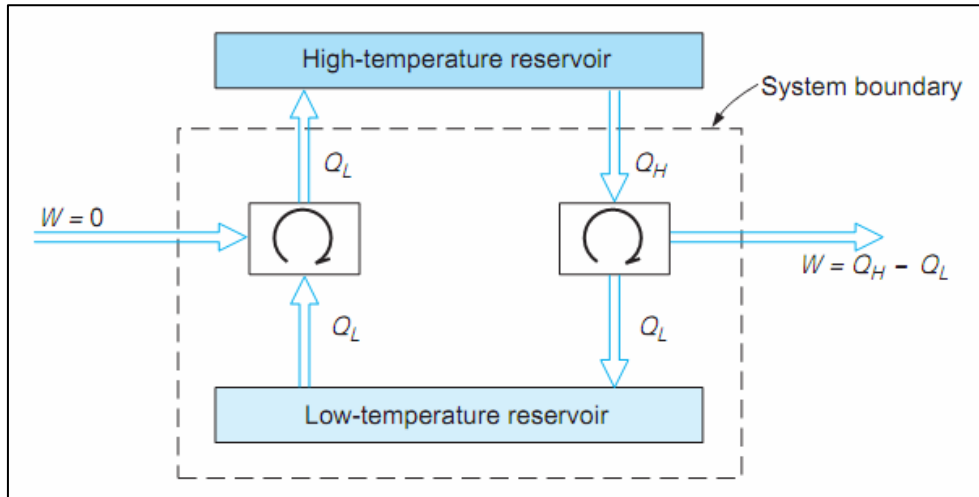
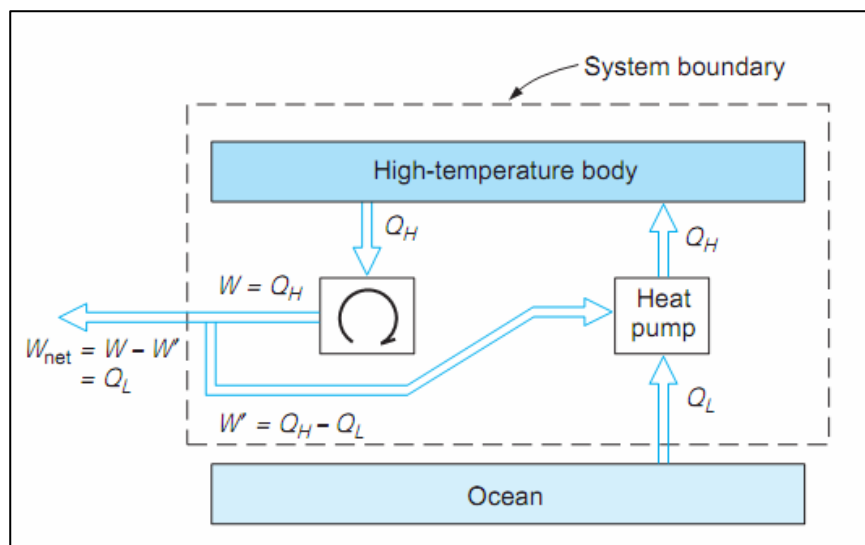


FIG.3 Demonstration of the equivalence of the two statements of the second law.

The third observation is that frequently the second law of thermodynamics has been stated as the impossibility of constructing a perpetual-motion machine of the second kind. A perpetual-motion machine of the first kind would create work from nothing or create mass or energy, thus violating the first law. A perpetual-motion machine of the second kind would extract heat from a source and then convert this heat completely into other forms of energy, thus violating the second law. A perpetual-motion machine of the third kind would have no friction, and thus would run indefinitely but produce no work. A heat engine that violated the second law could be made into a perpetual-motion machine of the second kind by taking the following steps. Consider Fig. 4, which might be the power plant of a ship. An amount of heat Q_L is transferred from the ocean to a high-temperature body by means of a heat pump. The work required is W^- , and the heat transferred to the high-temperature body is Q_H . Let the same amount of heat be transferred to a heat engine that violates the Kelvin–Planck statement of the second law and does an amount of work $W = Q_H$. Of this work, an amount $Q_H - Q_L$ is required to drive the heat pump, leaving the net work ($W_{\text{net}} = Q_L$) available for driving the ship. Thus, we have a perpetual-motion machine in the sense that work is done by utilizing freely available sources of energy such as the ocean or atmosphere.

FIG.4 A
perpetual-motion
machine of the second
kind



THE REVERSIBLE PROCESS

The question that can now logically be posed is this: If it is impossible to have a heat engine of 100% efficiency, what is the maximum efficiency one can have? The first step in the answer to this question is to define an ideal process, which is called a **reversible** process. A reversible process for a system is defined as a process that, once having taken place, can be reversed and in so doing leave no change in either system or surroundings. Consider first Fig.5, in which a gas, which we define as the system, is restrained at high pressure by a piston that is secured by a pin. When the pin is removed, the piston is raised and forced abruptly against the stops. Some work is done by the system, since the piston has been raised a certain amount. Suppose we wish to restore the system to its initial state. One way of doing this would be to exert a force on the piston and thus compress the gas until the pin can be reinserted in the piston. Since the pressure on the face of the piston is greater on the return stroke than on the initial stroke, the work done on the gas in this reverse process is greater than the work done by the gas in the initial process. An amount of heat must be transferred from the gas during the reverse stroke so that the system has the same internal energy as it had originally. Thus, the system is restored to its initial state, but the surroundings have changed by virtue of the fact that work was required to force the piston down and heat was transferred to the surroundings. The initial process therefore is *an irreversible* one because it could not be reversed without leaving a change in the surroundings.

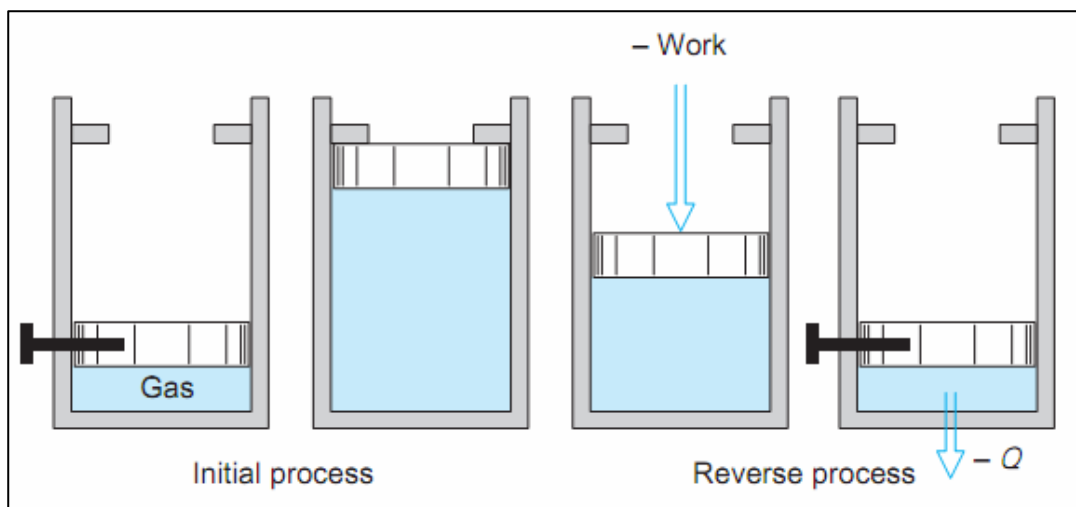


FIG.5 An example of an irreversible process.

Irreversibilities

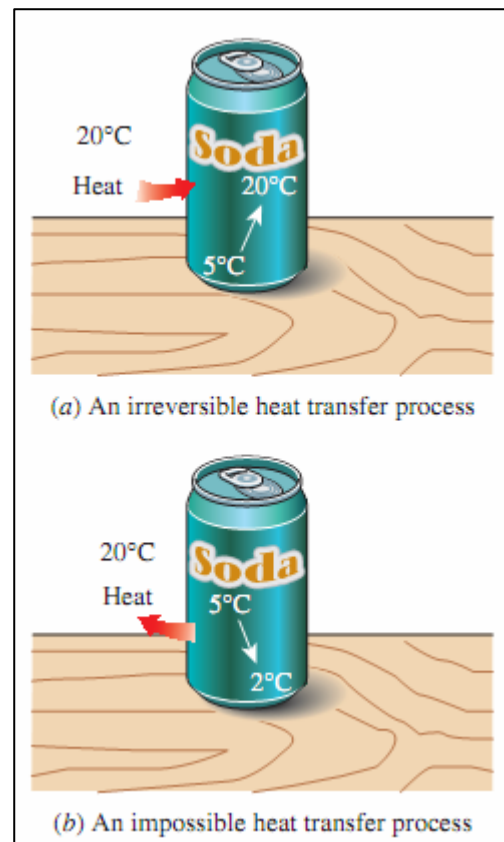
The factors that cause a process to be irreversible are called irreversibilities. They include friction, unrestrained expansion, mixing of two fluids, heat transfer across a finite temperature difference, electric resistance, inelastic deformation of solids, and chemical reactions. The presence of any of these effects renders a process irreversible. A reversible process involves none of these. Some of the frequently encountered irreversibilities are discussed briefly below.

The irreversibility familiar to us all is heat transfer through a finite temperature difference. Consider a can of cold soda left in a warm room (Fig.6). Heat is transferred from the warmer room air to the cooler soda. The only way this process can be reversed and the soda restored to its original temperature is to provide refrigeration, which requires some work input. At the end of the reverse process, the soda will be restored to its initial state, but the surroundings will not be. The internal energy of the surroundings will increase by an amount equal in magnitude to the work supplied to the refrigerator. The restoration of the surroundings to the initial state can be done only by converting this excess internal energy completely to work, which is impossible to do without violating the second law. Since only the system, not both the system and the surroundings, can be restored to its initial condition, heat transfer through a finite temperature difference is an irreversible process. Heat transfer can occur only when there is a temperature difference between a system and its surroundings. Therefore, it is physically impossible to have a reversible heat transfer process. But a heat transfer process becomes less and less irreversible as the temperature difference between the two bodies approaches zero. Then, heat transfer through a differential temperature difference dT can be considered to be reversible. As dT approaches zero, the process can be reversed in direction (at least theoretically) without requiring any refrigeration. Notice

that reversible heat transfer is a conceptual process and cannot be duplicated in the real world. The smaller the temperature difference between two bodies, the smaller the heat transfer rate will be. Any significant heat transfer through a small temperature difference requires a very large surface area and a very long time. Therefore, even though approaching reversible heat transfer is desirable from a thermodynamic point of view, it is impractical and not economically feasible.

FIG. 6

(a) Heat transfer through a temperature difference is irreversible, and (b) the reverse process is impossible.

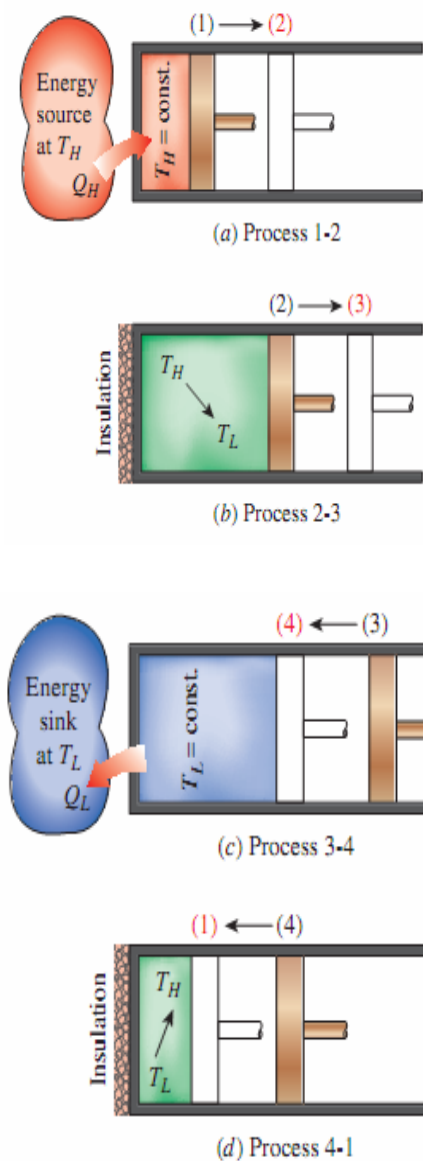


THE CARNOT CYCLE

The heat engines are cyclic devices and that the working fluid of a heat engine returns to its initial state at the end of each cycle. Work is done by the working fluid during one part of the cycle and on the working fluid during another part. The difference between these two is the net work delivered by the heat engine. The efficiency of a heat-engine cycle greatly depends on how the individual processes that make up the cycle are executed. The net work, thus the cycle efficiency, can be maximized by using processes that require the least amount of work and deliver the most, that is, by using reversible processes. Therefore, it is no surprise that the most efficient cycles are reversible cycles, that is, cycles that consist entirely of reversible processes. Reversible cycles cannot be achieved in practice because the irreversibilities associated with each process cannot be eliminated. However, reversible cycles provide upper limits on the performance of real cycles. Heat engines and refrigerators that work on reversible cycles serve as models to

which actual heat engines and refrigerators can be compared. Reversible cycles also serve as starting points in the development of actual cycles and are modified as needed to meet certain requirements.

Probably the best known reversible cycle is the Carnot cycle, first proposed in 1824 by French engineer Sadi Carnot. The theoretical heat engine that operates on the Carnot cycle is called the Carnot heat engine. The Carnot cycle is composed of four reversible processes—two isothermal and two adiabatic—and it can be executed either in a closed or a steady-flow system.



Reversible Isothermal Expansion (process 1-2, $T_H = \text{constant}$). Initially (state 1), the temperature of the gas is T_H and the cylinder head is in close contact with a source at temperature T_H . The gas is allowed to expand slowly, doing work on the surroundings. As the gas expands, the temperature of the gas tends to decrease. But as soon as the temperature drops by an infinitesimal amount dT , some heat is transferred from the reservoir into the gas, raising the gas temperature to T_H . Thus, the gas temperature is kept constant at T_H . Since the temperature difference between the gas and the reservoir never exceeds a differential amount dT , this is a reversible heat transfer process. It continues until the piston reaches position 2. The amount of total heat transferred to the gas during this process is Q_H .

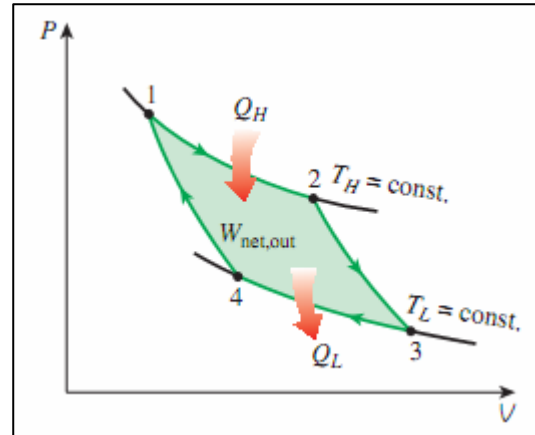
Reversible Adiabatic Expansion (process 2-3, temperature drops from T_H to T_L). At state 2, the reservoir that was in contact with the cylinder head is removed and replaced by insulation so that the system becomes adiabatic. The gas continues to expand slowly, doing work on the surroundings until its temperature drops from T_H to T_L (state 3). The piston is assumed to be frictionless and the process to be quasi-equilibrium, so the process is reversible as well as adiabatic.

Reversible Isothermal Compression (process 3-4, $T_L = \text{constant}$). At state 3, the insulation at the cylinder head is removed, and the cylinder is brought into contact with a sink at temperature T_L . Now the piston is pushed inward by an external force, doing work on the gas. As the gas is compressed, its temperature tends to rise. But as soon as it rises by an infinitesimal amount dT , heat is transferred from the gas to the sink, causing the gas temperature to drop to T_L . Thus, the gas temperature remains constant at T_L . Since the temperature difference between the gas and the sink never exceeds a differential amount dT , this is a reversible heat transfer process. It continues until the piston reaches state 4. The amount of heat rejected from the gas during this process is Q_L .

Reversible Adiabatic Compression (process 4-1, temperature rises from T_L to T_H). State 4 is such that when the low-temperature reservoir is removed, the insulation is put back on the cylinder head, and the gas is compressed in a reversible manner, the gas returns to its initial state (state 1). The temperature rises from T_L to T_H during this reversible adiabatic compression process, which completes the cycle.

The P-V diagram of this cycle is shown in Fig.7. Remembering that on a P-V diagram the area under the process curve represents the boundary work for quasi-equilibrium (internally reversible) processes, we see that the area under curve 1-2-3 is the work done by the gas during the expansion part of the cycle, and the area under curve 3-4-1 is the work done on the gas during the compression part of the cycle. The area enclosed by the path of the cycle (area 1-2-3-4-1) is the difference between these two and represents the net work done during the cycle.

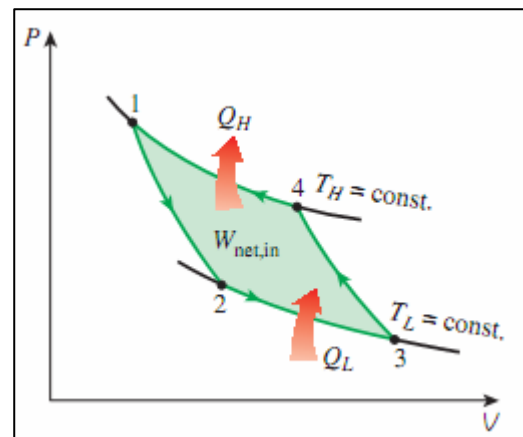
FIGURE 7
P-V diagram of the Carnot cycle.



The Reversed Carnot Cycle

The Carnot heat-engine cycle just described is a totally reversible cycle. Therefore, all the processes that comprise it can be reversed, in which case it becomes the Carnot refrigeration cycle. This time, the cycle remains exactly the same, except that the directions of any heat and work interactions are reversed: Heat in the amount of Q_L is absorbed from the low-temperature reservoir, heat in the amount of Q_H is rejected to a high-temperature reservoir, and a work input of $W_{\text{net,in}}$ is required to accomplish all this. The P-V diagram of the reversed Carnot cycle is the same as the one given for the Carnot cycle, except that the directions of the processes are reversed, as shown in Fig. 8.

FIG.8
P-V diagram of the reversed Carnot cycle



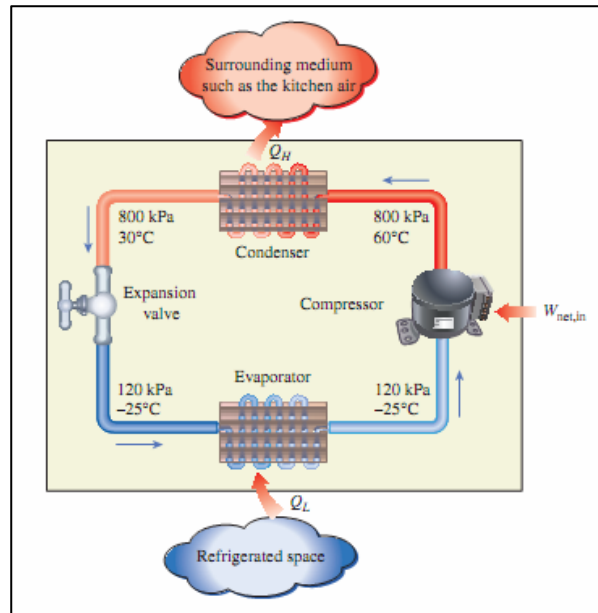
REFRIGERATORS AND HEAT PUMPS

The heat is transferred in the direction of decreasing temperature, that is, from high-temperature mediums to low-temperature ones. This heat transfer process occurs in nature without requiring any devices. The reverse process, however, cannot occur by itself.

The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called refrigerators. Refrigerators, like heat engines, are cyclic devices. The working fluid used in the refrigeration cycle is called a refrigerant. The most frequently used refrigeration cycle is the vapor-compression refrigeration cycle, which involves four main components: a compressor, a condenser, an expansion valve, and an evaporator, as shown in Fig. 9.

FIG.9

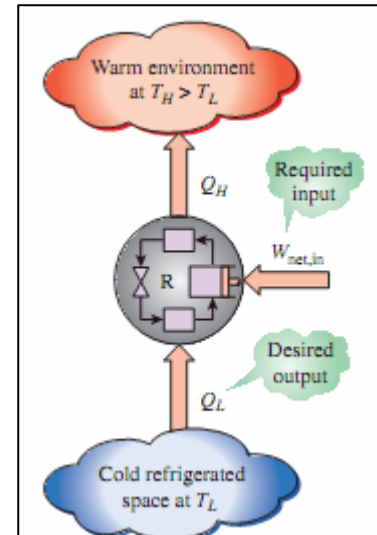
Basic components of a refrigeration system and typical operating conditions.



A refrigerator is shown schematically in Fig. 10. Here Q_L is the magnitude of the heat removed from the refrigerated space at temperature T_L , Q_H is the magnitude of the heat rejected to the warm environment at temperature T_H , and $W_{\text{net,in}}$ is the net work input to the refrigerator. As discussed before, Q_L and Q_H represent magnitudes and thus are positive quantities.

FIG.10

The objective of a refrigerator is to remove Q_L from the cooled space.



Coefficient of Performance

The efficiency of a refrigerator is expressed in terms of the coefficient of performance (COP), denoted by COP_R . The objective of a refrigerator is to remove heat (Q_L) from the refrigerated space. To accomplish this objective, it requires a work input of $W_{net,in}$. Then the COP of a refrigerator can be expressed as

$$COP_R = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{W_{net,in}}$$

This relation can also be expressed in rate form by replacing Q_L by \dot{Q}_L and $W_{net,in}$ by $\dot{W}_{net,in}$.

The conservation of energy principle for a cyclic device requires that

$$W_{net,in} = Q_H - Q_L \quad (\text{kJ})$$

Then the COP relation becomes

$$COP_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$

Heat Pumps

Another device that transfers heat from a low-temperature medium to a high temperature one is the heat pump, shown schematically in Fig.11. Refrigerators and heat pumps operate on the same cycle but differ in their objectives. The objective of a refrigerator is to maintain the refrigerated space at a low temperature by removing heat from it. Discharging this heat to a higher-temperature medium is merely a necessary part of the operation, not the purpose. The objective of a heat pump, however, is to maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low-

temperature source, such as well water or cold outside air in winter, and supplying this heat to the high-temperature medium such as a house (Fig. 12). An ordinary refrigerator that is placed in the window of a house with its door open to the cold outside air in winter will function as a heat pump since it will try to cool the outside by absorbing heat from it and rejecting this heat into the house through the coils behind it. The measure of performance of a heat pump is also expressed in terms of the coefficient of performance COP_{HP}, defined as

$$\text{COP}_{\text{HP}} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_H}{W_{\text{net,in}}}$$

which can also be expressed as

$$\text{COP}_{\text{HP}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$

$$\text{COP}_{\text{HP}} = \text{COP}_R + 1$$

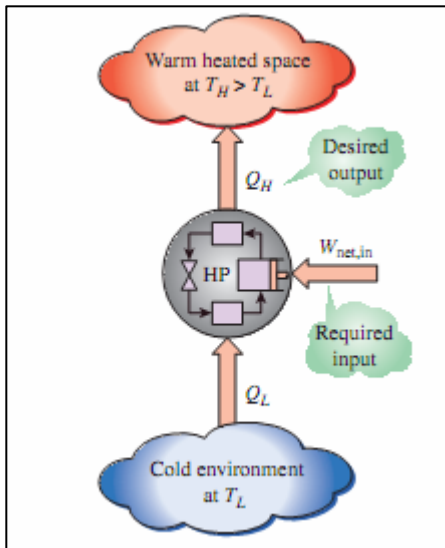


FIG.11

The objective of a heat pump is to supply heat Q_H into the warmer space

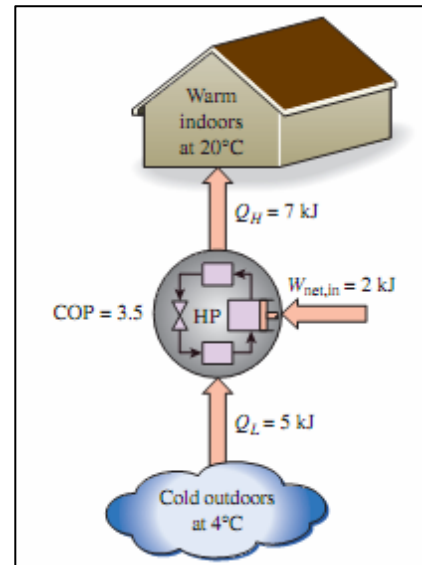


FIG.12

The work supplied to a heat pump is used to extract energy from the cold outdoors and carry it into the warm indoors.

Ex.1 The food compartment of a refrigerator, shown in Fig., is maintained at 4°C by removing heat from it at a rate of 360 kJ/min. If the required power input to the refrigerator is 2 kW, determine (a) the coefficient of performance of the refrigerator and (b) the rate of heat rejection to the room that houses the refrigerator

SOLUTION The power consumption of a refrigerator is given. The COP and the rate of heat rejection are to be determined.

Assumptions Steady operating conditions exist.

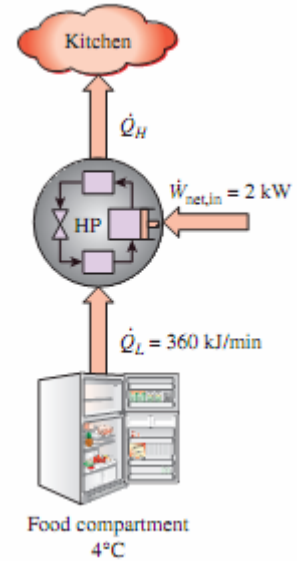
Analysis (a) The coefficient of performance of the refrigerator is

$$\text{COP}_R = \frac{\dot{Q}_L}{\dot{W}_{\text{net},\text{in}}} = \frac{360 \text{ kJ/min}}{2 \text{ kW}} \left(\frac{1 \text{ kW}}{60 \text{ kJ/min}} \right) = 3$$

That is, 3 kJ of heat is removed from the refrigerated space for each kJ of work supplied.

(b) The rate at which heat is rejected to the room that houses the refrigerator is determined from the conservation of energy relation for cyclic devices,

$$\dot{Q}_H = \dot{Q}_L + \dot{W}_{\text{net},\text{in}} = 360 \text{ kJ/min} + (2 \text{ kW}) \left(\frac{60 \text{ kJ/min}}{1 \text{ kW}} \right) = 480 \text{ kJ/min}$$



Ex.2 A heat pump is used to meet the heating requirements of a house and maintain it at 20°C. On a day when the outdoor air temperature drops to -22°C, the house is estimated to lose heat at a rate of 80,000 kJ/h. If the heat pump under these conditions has a COP of 2.5, determine (a) the power consumed by the heat pump and (b) the rate at which heat is absorbed from the cold outdoor air.

SOLUTION The COP of a heat pump is given. The power consumption and the rate of heat absorption are to be determined.

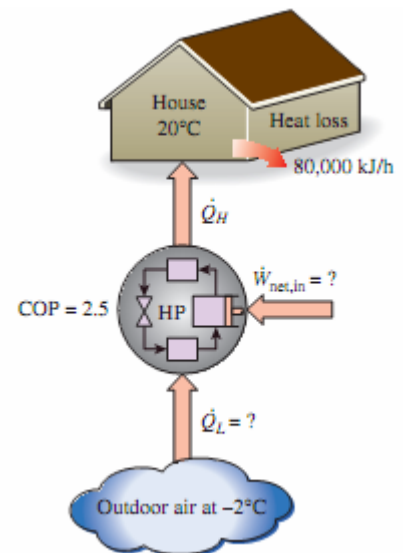
Assumptions Steady operating conditions exist.

Analysis (a) The power consumed by this heat pump, is determined from the definition of the coefficient of performance to be

$$\dot{W}_{\text{net},\text{in}} = \frac{\dot{Q}_H}{\text{COP}_{\text{HP}}} = \frac{80,000 \text{ kJ/h}}{2.5} = 32,000 \text{ kJ/h (or 8.9 kW)}$$

(b) The house is losing heat at a rate of 80,000 kJ/h. If the house is to be maintained at a constant temperature of 20°C, the heat pump must deliver heat to the house at the same rate, that is, at a rate of 80,000 kJ/h. Then the rate of heat transfer from the outdoor becomes

$$\dot{Q}_L = \dot{Q}_H - \dot{W}_{\text{net},\text{in}} = (80,000 - 32,000) \text{ kJ/h} = 48,000 \text{ kJ/h}$$



Ex.3 Let us consider the heat engine, shown schematically in Fig., that receives a heat transfer rate of 1 MW at a high temperature of 550°C and rejects energy to the ambient surroundings at 300 K. Work is produced at a rate of 450 kW. We would like to know how much energy is discarded to the ambient surroundings and the engine efficiency and compare both of these to a Carnot heat engine operating between the same two reservoirs.

Solution

If we take the heat engine as a control volume, the energy equation gives

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = 1000 - 450 = 550 \text{ kW}$$

and from the definition of efficiency

$$\eta_{\text{thermal}} = \dot{W} / \dot{Q}_H = 450 / 1000 = 0.45$$

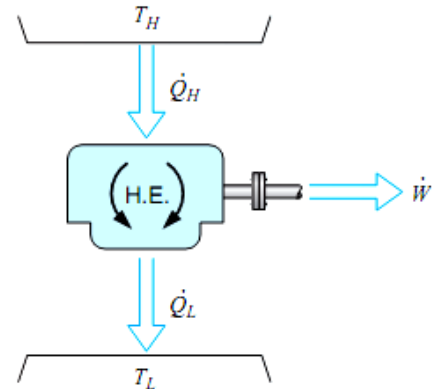
For the Carnot heat engine, the efficiency is given by the temperature of the reservoirs:

$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H} = 1 - \frac{300}{550 + 273} = 0.635$$

The rates of work and heat rejection become

$$\dot{W} = \eta_{\text{Carnot}} \dot{Q}_H = 0.635 \times 1000 = 635 \text{ kW}$$

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = 1000 - 635 = 365 \text{ kW}$$



THE CARNOT REFRIGERATOR AND HEAT PUMP

A refrigerator or a heat pump that operates on the reversed Carnot cycle is called a Carnot refrigerator, or a Carnot heat pump. The coefficient of performance of any refrigerator or heat pump, reversible or irreversible, is given

$$\text{COP}_R = \frac{1}{Q_H/Q_L - 1} \quad \text{and} \quad \text{COP}_{\text{HP}} = \frac{1}{1 - Q_L/Q_H}$$

where Q_L is the amount of heat absorbed from the low-temperature medium and Q_H is the amount of heat rejected to the high-temperature medium. The **COPs** of all reversible refrigerators or heat pumps can be determined by replacing the heat transfer ratios in the above relations by the ratios of the absolute temperatures of the high- and low-temperature reservoirs

$$\text{COP}_{R,\text{rev}} = \frac{1}{T_H/T_L - 1}$$

and

$$\text{COP}_{\text{HP},\text{rev}} = \frac{1}{1 - T_L/T_H}$$

The coefficients of performance of actual and reversible refrigerators operating between the same temperature limits can be compared as follows:

$$\text{COP}_R \begin{cases} < \text{COP}_{R,\text{rev}} & \text{irreversible refrigerator} \\ = \text{COP}_{R,\text{rev}} & \text{reversible refrigerator} \\ > \text{COP}_{R,\text{rev}} & \text{impossible refrigerator} \end{cases}$$

Ex.4 A Carnot refrigeration cycle is executed in a closed system in the saturated liquid–vapor mixture region using 0.8 kg of refrigerant-134a as the working fluid (Fig.). The maximum and the minimum temperatures in the cycle are 20 and -8°C, respectively. It is known that the refrigerant is saturated liquid at the end of the heat rejection process, and the net work input to the cycle is 15 kJ. Determine the fraction of the mass of the refrigerant that vaporizes during the heat addition process, and the pressure at the end of the heat rejection process

Analysis Knowing the high and low temperatures, the coefficient of performance of the cycle is

$$\text{COP}_R = \frac{1}{T_H/T_L - 1} = \frac{1}{(20 + 273 \text{ K})/(-8 + 273 \text{ K}) - 1} = 9.464$$

The amount of cooling is determined from the definition of the coefficient of performance to be

$$Q_L = \text{COP}_R \times W_{\text{in}} = (9.464)(15 \text{ kJ}) = 142 \text{ kJ}$$

The enthalpy of vaporization R-134a at -8°C is $h_{fg} = 204.59 \text{ kJ/kg}$ (Table A-11). Then the amount of refrigerant that vaporizes during heat absorption becomes

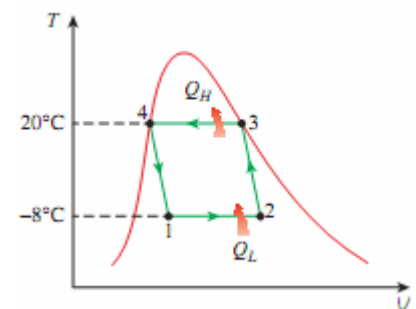
$$Q_L = m_{\text{evap}} h_{fg@-8^\circ\text{C}} \rightarrow m_{\text{evap}} = \frac{142 \text{ kJ}}{204.59 \text{ kJ/kg}} = 0.694 \text{ kg}$$

Therefore, the fraction of mass that vaporized during heat addition process to the refrigerant is

$$\text{Mass fraction} = \frac{m_{\text{evap}}}{m_{\text{total}}} = \frac{0.694 \text{ kg}}{0.8 \text{ kg}} = 0.868 \text{ or } 86.8\%$$

The pressure at the end of heat rejection process is simply the saturation pressure at heat rejection temperature,

$$P_4 = P_{\text{sat}@20^\circ\text{C}} = 572.1 \text{ kPa}$$



Entropy

The first law of thermodynamics deals with the *property energy* and the conservation of it. The second law leads to the definition of a new property called *entropy* (S). Entropy is a somewhat abstract property, and it is difficult to give a physical description of it without considering the microscopic state of the system.

The first step in our consideration of the property we call entropy is to establish the inequality of Clausius, which is

$$\oint \frac{\delta Q}{T} \leq 0$$

Consider first a reversible (Carnot) heat engine cycle operating between reservoirs at temperatures T_H and T_L , as shown in Fig.1. For this cycle, the cyclic integral of the heat transfer, $\oint \delta Q$, is greater than zero

$$\oint \delta Q = Q_H - Q_L > 0$$

Since T_H and T_L are constant, from the definition of the absolute temperature scale and from the fact that this is a reversible cycle, it follows that

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

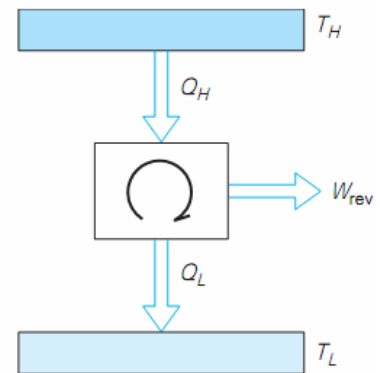


FIG.1
Reversible heat engine
cycle for demonstration
of the inequality of
Clausius.

If $\oint \delta Q$, the cyclic integral of δQ , approaches zero (by making T_H approach T_L) and the cycle remains reversible, the cyclic integral of $\delta Q/T$ remains zero. Thus, we conclude that for all reversible heat engine cycles

$$\oint \delta Q \geq 0$$

and

$$\oint \frac{\delta Q}{T} = 0$$

Now consider an irreversible cyclic heat engine operating between the same T_H and T_L as the reversible engine of Fig.1 and receiving the same quantity of heat Q_H . Comparing the irreversible cycle with the reversible one, we conclude from the second law that

$$W_{\text{irr}} < W_{\text{rev}}$$

Since $Q_H - Q_L = W$ for both the reversible and irreversible cycles, we conclude that

$$Q_H - Q_{L \text{ irr}} < Q_H - Q_{L \text{ rev}}$$

and therefore

$$Q_{L \text{ irr}} > Q_{L \text{ rev}}$$

Consequently, for the irreversible cyclic engine,

$$\oint \delta Q = Q_H - Q_{L \text{ irr}} > 0$$

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_{L \text{ irr}}}{T_L} < 0$$

Suppose that we cause the engine to become more and more irreversible but keep Q_H , T_H , and T_L fixed. The cyclic integral of δQ then approaches zero, and that for $\delta Q/T$ becomes a progressively larger negative value. In the limit, as the work output goes to zero,

$$\oint \delta Q = 0$$

$$\oint \frac{\delta Q}{T} < 0$$

Thus, we conclude that for all irreversible heat engine cycles

$$\oint \delta Q \geq 0$$

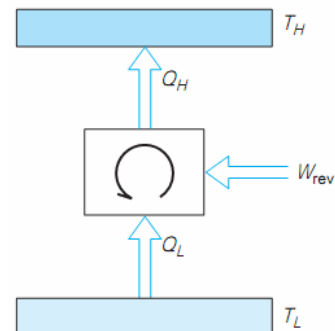
$$\oint \frac{\delta Q}{T} < 0$$

To complete the demonstration of the inequality of Clausius, we must perform similar analyses for both reversible and irreversible refrigeration cycles. For the reversible refrigeration cycle shown in Fig.2,

$$\oint \delta Q = -Q_H + Q_L < 0$$

and

$$\oint \frac{\delta Q}{T} = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$$



As the cyclic integral of δQ approaches zero reversibly (T_H approaches T_L), the cyclic integral of $\delta Q/T$ remains at zero. In the limit,

$$\oint \delta Q = 0$$

$$\oint \frac{\delta Q}{T} = 0$$

Thus, for all reversible refrigeration cycles,

$$\oint \delta Q \leq 0$$

$$\oint \frac{\delta Q}{T} = 0$$

Finally, let an irreversible cyclic refrigerator operate between temperatures T_H and T_L and receive the same amount of heat Q_L as the reversible refrigerator of Fig.2. From the second law, we conclude that the work input required will be greater for the irreversible refrigerator, or

$$W_{\text{irr}} > W_{\text{rev}}$$

Since $Q_H - Q_L = W$ for each cycle, it follows that

$$Q_{H \text{ irr}} - Q_L > Q_{H \text{ rev}} - Q_L$$

and therefore,

$$Q_{H \text{ irr}} > Q_{H \text{ rev}}$$

That is, the heat rejected by the irreversible refrigerator to the high-temperature reservoir is greater than the heat rejected by the reversible refrigerator. Therefore, for the irreversible refrigerator

$$\oint \delta Q = -Q_{H \text{ irr}} + Q_L < 0$$

$$\oint \frac{\delta Q}{T} = -\frac{Q_{H \text{ irr}}}{T_H} + \frac{Q_L}{T_L} < 0$$

As we make this machine progressively more irreversible but keep Q_L , T_H , and T_L constant, the cyclic integrals of δQ and $\delta Q/T$ both become larger in the negative direction. Consequently, a limiting case as the cyclic integral of δQ approaches zero does not exist for the irreversible refrigerator. Thus, for all irreversible refrigeration cycles,

$$\oint \delta Q < 0$$

$$\oint \frac{\delta Q}{T} < 0$$

The significance of the inequality of Clausius may be illustrated by considering the simple steam power plant cycle shown in Fig.3. This cycle is slightly different from the usual cycle for steam power plants in that the pump handles a mixture of liquid and vapor in such proportions that saturated liquid leaves the pump and enters the boiler. Suppose that someone reports that the pressure and quality at various points in the cycle are as given in Fig.3. Does this cycle satisfy the inequality of Clausius?

Heat is transferred in two places, the boiler and the condenser. Therefore,

$$\oint \frac{\delta Q}{T} = \int \left(\frac{\delta Q}{T} \right)_{\text{boiler}} + \int \left(\frac{\delta Q}{T} \right)_{\text{condenser}}$$

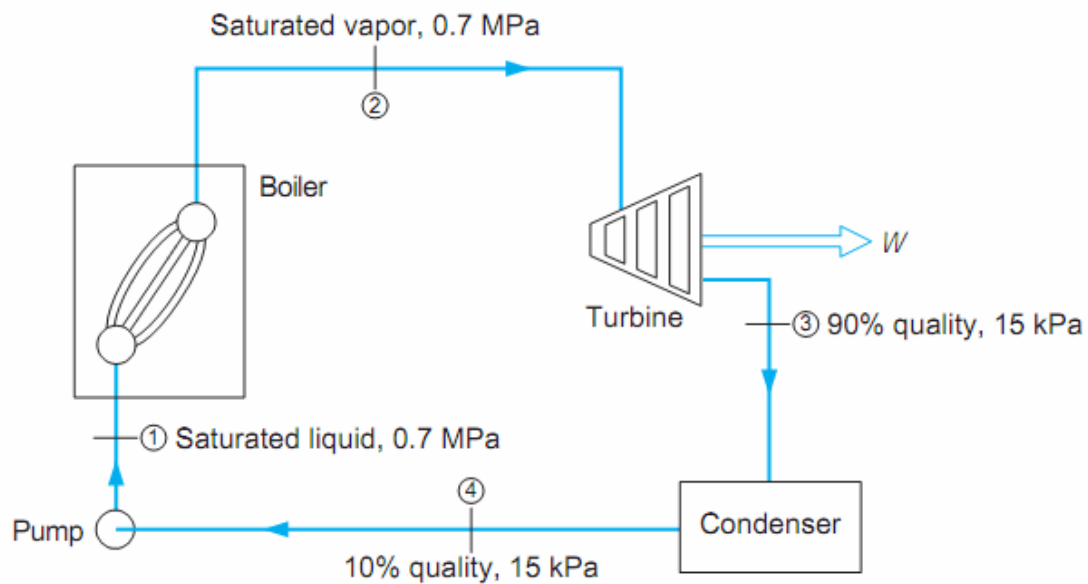


FIG.3 A simple steam power plant that demonstrates the inequality of Clausius.

Since the temperature remains constant in both the boiler and condenser, this may be integrated as follows:

$$\oint \frac{\delta Q}{T} = \frac{1}{T_1} \int_1^2 \delta Q + \frac{1}{T_3} \int_3^4 \delta Q = \frac{{}_1Q_2}{T_1} + \frac{{}_3Q_4}{T_3}$$

Let us consider a 1 kg mass as the working fluid. We have then

$${}_1q_2 = h_2 - h_1 = 2066.3 \text{ kJ/kg}, \quad T_1 = 164.97^\circ \text{C}$$

$${}_3q_4 = h_4 - h_3 = 463.4 - 2361.8 = -1898.4 \text{ kJ/kg}, \quad T_3 = 53.97^\circ \text{C}$$

Therefore,

$$\oint \frac{\delta Q}{T} = \frac{2066.3}{164.97 + 273.15} - \frac{1898.4}{53.97 + 273.15} = -1.087 \text{ kJ/kg K}$$

Thus, this cycle satisfies the inequality of Clausius, which is equivalent to saying that it does not violate the second law of thermodynamics.

ENTROPY—A PROPERTY OF A SYSTEM

The Fig.4, we can demonstrate that the second law of thermodynamics leads to a property of a system that we call entropy. Let a system (control mass) undergo a reversible process from state 1 to state 2 along a path A, and let the cycle be completed along path B, which is also reversible.

Because this is a reversible cycle, we can write

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left(\frac{\delta Q}{T} \right)_A + \int_2^1 \left(\frac{\delta Q}{T} \right)_B$$

Now consider another reversible cycle, which proceeds first along path C and is then completed along path B. For this cycle we can write

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left(\frac{\delta Q}{T} \right)_C + \int_2^1 \left(\frac{\delta Q}{T} \right)_B$$

Subtracting the second equation from the first, we have

$$\int_1^2 \left(\frac{\delta Q}{T} \right)_A = \int_1^2 \left(\frac{\delta Q}{T} \right)_C$$

Since $\oint \delta Q / T$ is the same for all reversible paths between states 1 and 2, we conclude that this quantity is independent of the path and is a function of the end states only; it is therefore a property. This property is called **entropy** and is designated S . It follows that entropy may be defined as a property of a substance in accordance with the relation

$$dS \equiv \left(\frac{\delta Q}{T} \right)_{\text{rev}}$$

Entropy is an extensive property, and the entropy per unit mass is designated s . It is important to note that entropy is defined here in terms of a reversible process.

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{rev}}$$

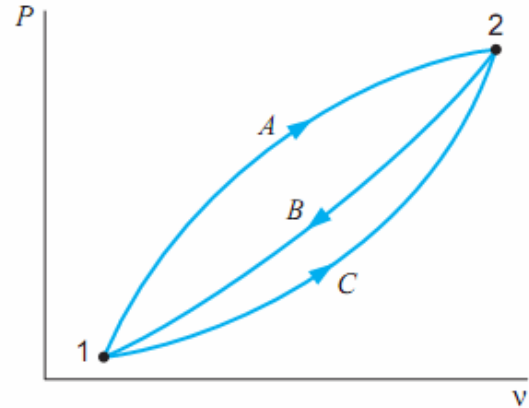


FIG. Two reversible cycles demonstrating that entropy is a property of a substance.

The thermodynamic properties of a substance are often shown on a temperature–entropy diagram and on an enthalpy–entropy diagram, which is also called a Mollier diagram, after Richard Mollier (1863–1935) of Germany. Figs.5 and 6 show the essential elements of temperature–entropy and enthalpy–entropy diagrams for steam. The general features of such diagrams are the same for all pure substances.

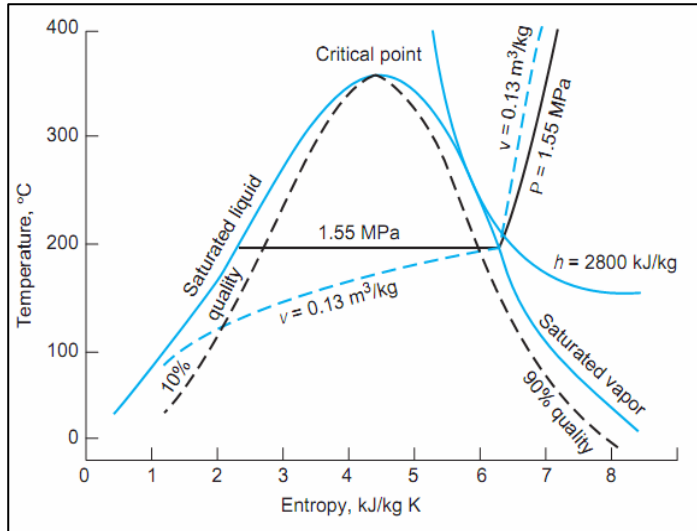


FIG.5
Temperature–entropy diagram for steam

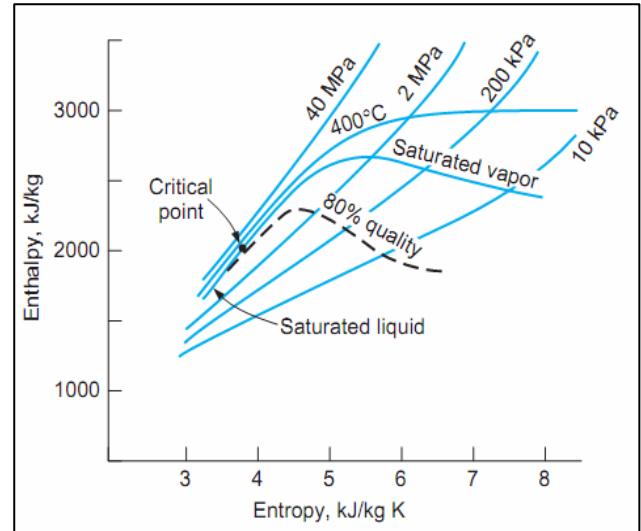


FIG.6
Enthalpy–entropy diagram for steam

ENTROPY CHANGE IN REVERSIBLE PROCESSES

Let the working fluid of a heat engine operating on the Carnot cycle make up the system. The first process is the isothermal transfer of heat to the working fluid from the high-temperature reservoir. For this process we can write:-

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{rev}}$$

Since this is a reversible process in which the temperature of the working fluid remains constant, the equation can be integrated to give

$$S_2 - S_1 = \frac{1}{T_H} \int_1^2 \delta Q = \frac{Q_H}{T_H}$$

This process is shown in Fig. 7a, and the area under line 1-2, area 1-2-b-a-1, represents the heat transferred to the working fluid during the process.

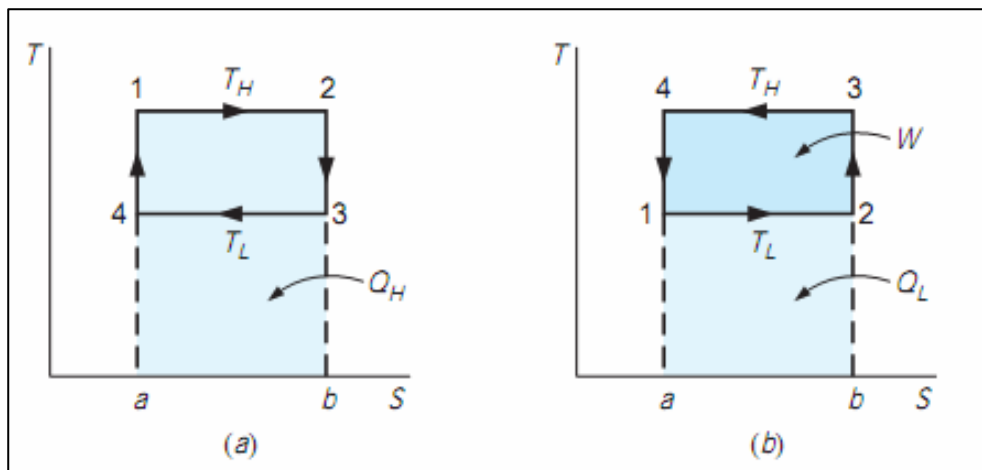


FIG.7 The Carnot cycle on the temperature-entropy diagram

The second process of a Carnot cycle is a reversible adiabatic one. From the definition of entropy,

$$dS = \left(\frac{\delta Q}{T} \right)_{\text{rev}}$$

it is evident that the entropy remains constant in a reversible adiabatic process. A constant-entropy process is called an isentropic process. Line 2-3 represents this process, and this process is concluded at state 3 when the temperature of the working fluid reaches T_L . The third process is the reversible isothermal process in which heat is transferred from the working fluid to the low-temperature reservoir. For this process we can write

$$S_4 - S_3 = \int_3^4 \left(\frac{\delta Q}{T} \right)_{\text{rev}} = \frac{Q_L}{T_L}$$

Since the net work of the cycle is equal to the net heat transfer, area 1–2–3–4–1 must represent the net work of the cycle. The efficiency of the cycle may also be expressed in terms of areas:

$$\eta_{th} = \frac{W_{net}}{Q_H} = \frac{\text{area } 1-2-3-4-1}{\text{area } 1-2-b-a-1}$$

Some statements made earlier about efficiencies may now be understood graphically. For example, increasing T_H while T_L remains constant increases the efficiency. Decreasing T_L while T_H remains constant increases the efficiency. It is also evident that the efficiency approaches 100% as the absolute temperature at which heat is rejected approaches zero.

If the cycle is reversed, we have a refrigerator or heat pump. The Carnot cycle for a refrigerator is shown in Fig. 7b. Notice that the entropy of the working fluid increases at T_L , since heat is transferred to the working fluid at T_L . The entropy decreases at T_H because of heat transfer from the working fluid.

Since this is a constant-pressure process, the heat transfer per unit mass is equal to h_{fg} . Thus,

$$s_2 - s_1 = s_{fg} = \frac{1}{m} \int_1^2 \left(\frac{\delta Q}{T} \right)_{rev} = \frac{1}{mT} \int_1^2 \delta Q = \frac{q_2}{T} = \frac{h_{fg}}{T}$$

This relation gives a clue about how s_{fg} is calculated for tabulation in tables of thermodynamic properties. For example, consider steam at 10 MPa. From the steam tables we have

$$h_{fg} = 1317.1 \text{ kJ/kg}$$

$$T = 311.06 + 273.15 = 584.21 \text{ K}$$

Therefore,

$$s_{fg} = \frac{h_{fg}}{T} = \frac{1317.1}{584.21} = 2.2544 \text{ kJ/kg K}$$

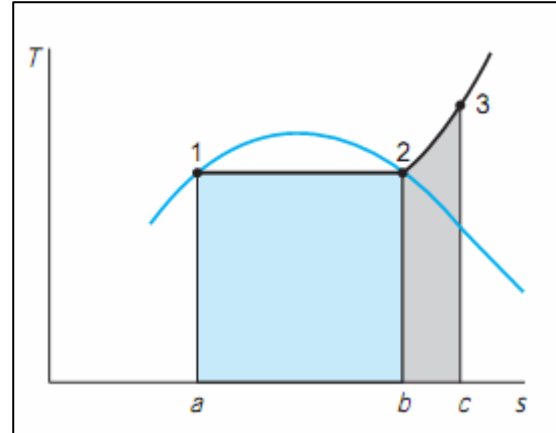
This is the value listed for s_{fg} in the steam tables.

This process would correspond to process 1–2 on the T–s diagram of Fig. 8 (note that absolute temperature is required here), and area 1–2–b–a–1 represents the heat transfer.

$${}_2q_3 = \frac{1}{m} \int_2^3 \delta Q = \int_2^3 T ds$$

Since T is not constant, this equation cannot be integrated unless we know a relation between temperature and entropy. However, we do realize that the area under line 2–3, area 2–3–c–b–2, represents $\int_2^3 T ds$ and therefore represents the heat transferred during this reversible process.

FIG.8 A
temperature–entropy
diagram showing areas
that represent heat
transfer for an internally
reversible process.



EX.1 Consider a Carnot-cycle heat pump with R-134a as the working fluid. Heat is absorbed into the R-134a at 0°C, during which process it changes from a two-phase state to saturated vapor. The heat is rejected from the R-134a at 60° C and ends up as saturated liquid. Find the pressure after compression, before the heat rejection process, and determine the COP for the cycle.

Solution

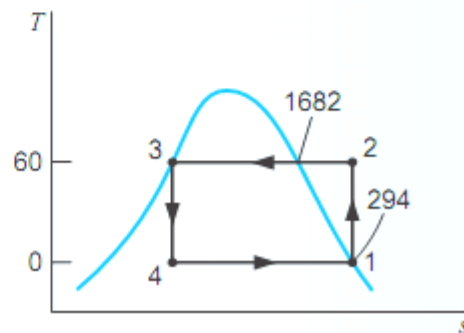
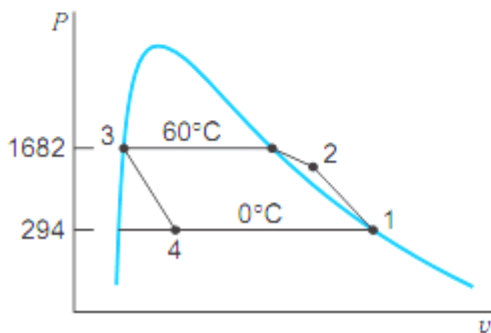
From the definition of the Carnot cycle, we have two constant-temperature (isothermal) processes that involve heat transfer and two adiabatic processes in which the temperature changes. The variation in s follows

$$ds = \delta q / T$$

State 4 Table B.5.1: $s_4 = s_3 = s_f@60\text{deg} = 1.2857 \text{ kJ/kg K}$

State 1 Table B.5.1: $s_1 = s_2 = s_g@0\text{deg} = 1.7262 \text{ kJ/kg K}$

State 2 Table B.5.2: $60^\circ \text{C}, s_2 = s_1 = s_g@0\text{deg}$



Interpolate between 1400 kPa and 1600 kPa

$$P_2 = 1400 + (1600 - 1400) \frac{1.7262 - 1.736}{1.7135 - 1.736} = 1487.1 \text{ kPa}$$

From the fact that it is a Carnot cycle the COP becomes,

$$\text{COP} = \frac{q_H}{w_{\text{IN}}} = \frac{T_H}{T_H - T_L} = \frac{333.15}{60} = 5.55$$

THE THERMODYNAMIC PROPERTY RELATION

At this point we derive two important thermodynamic relations for a simple compressible substance. These relations are

$$T dS = dU + P dV$$

$$T dS = dH - V dP$$

The first of these relations can be derived by considering a simple compressible substance in the absence of motion or gravitational effects. The first law for a change of state under these conditions can be written

$$\delta Q = dU + \delta W$$

The changes of state in which the state of the substance can be identified at all times. Thus, we must consider a quasi-equilibrium process or, to use the term introduced in the previous chapter, a reversible process. For a reversible process of a simple compressible substance, can write

$$\delta Q = T dS \quad \text{and} \quad \delta W = P dV$$

Substituting these relations into the first-law equation, we have

$$T dS = dU + P dV$$

Since enthalpy is defined as

$$H = U + PV$$

it follows that

$$dH = dU + P dV + V dP$$

Substituting this relation into Eq. 8.5, we have

$$T dS = dH - V dP$$

These equations can also be written for a unit mass:

$$T ds = du + P dv$$

$$T ds = dh - v dP$$

ENTROPY CHANGE OF A SOLID OR LIQUID

Considered the calculation of the internal energy and enthalpy changes with temperature for solids and liquids and found that, in general, it is possible to express both in terms of the specific heat.

to calculate the entropy change for a solid or liquid. Note that for such a phase the specific volume term in

$$ds \simeq \frac{du}{T} \simeq \frac{C}{T} dT$$

Now, as was mentioned in Section 5.6, for many processes involving a solid or liquid, we may assume that the specific heat remains constant, The result is

$$s_2 - s_1 \simeq C \ln \frac{T_2}{T_1}$$

If the specific heat is not constant, then commonly C is known as a function of T .

EX.2 One kilogram of liquid water is heated from 20° C to 90° C. Calculate the entropy change, assuming constant specific heat, and compare the result with that found when using the steam tables.

Solution

For constant specific heat,

$$s_2 - s_1 = 4.184 \ln \left(\frac{363.2}{293.2} \right) = 0.8958 \text{ kJ/kg K}$$

Comparing this result with that obtained by using the steam tables, we have

$$\begin{aligned} s_2 - s_1 &= s_{f 90^\circ \text{C}} - s_{f 20^\circ \text{C}} = 1.1925 - 0.2966 \\ &= 0.8959 \text{ kJ/kg K} \end{aligned}$$

ENTROPY CHANGE OF AN IDEAL GAS

Two very useful equations for computing the entropy change of an ideal gas can be developed

$$T ds = du + P dv$$

For an ideal gas

$$du = C_{v0} dT \quad \text{and} \quad \frac{P}{T} = \frac{R}{v}$$

Therefore,

$$ds = C_{v0} \frac{dT}{T} + \frac{R dv}{v}$$

$$s_2 - s_1 = \int_1^2 C_{v0} \frac{dT}{T} + R \ln \frac{v_2}{v_1}$$

Similarly,

$$T ds = dh - v dP$$

For an ideal gas

$$dh = C_{p0} dT \quad \text{and} \quad \frac{v}{T} = \frac{R}{P}$$

Therefore,

$$ds = C_{p0} \frac{dT}{T} - R \frac{dP}{P}$$

$$s_2 - s_1 = \int_1^2 C_{p0} \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

Again, there are three possibilities to examine, the simplest of which is the assumption of constant specific heat. In this instance it is possible

$$s_2 - s_1 = C_{p0} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Similarly, integrating

$$s_2 - s_1 = C_{v0} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

The second possibility for the specific heat is to use an analytical equation for C_p as a function of temperature, for example, one of those listed in Table A.6.

The third possibility is to integrate the results of the calculations of statistical thermodynamics from reference temperature T_0 to any other temperature T and define the standard entropy:-

$$s_T^0 = \int_{T_0}^T \frac{C_{p0}}{T} dT$$

The entropy change between any two states 1 and 2 is then given by

$$s_2 - s_1 = (s_{T2}^0 - s_{T1}^0) - R \ln \frac{P_2}{P_1}$$

TABLE A.6

Constant-Pressure Specific Heats of Various Ideal Gases[†]

		$C_{p0} = C_0 + C_1\theta + C_2\theta^2 + C_3\theta^3$ (kJ/kg K)		$\theta = T(\text{Kelvin})/1000$	
Gas	Formula	C_0	C_1	C_2	C_3
Steam	H ₂ O	1.79	0.107	0.586	-0.20
Acetylene	C ₂ H ₂	1.03	2.91	-1.92	0.54
Air	—	1.05	-0.365	0.85	-0.39
Ammonia	NH ₃	1.60	1.4	1.0	-0.7
Argon	Ar	0.52	0	0	0
Butane	C ₄ H ₁₀	0.163	5.70	-1.906	-0.049
Carbon dioxide	CO ₂	0.45	1.67	-1.27	0.39
Carbon monoxide	CO	1.10	-0.46	1.0	-0.454
Ethane	C ₂ H ₆	0.18	5.92	-2.31	0.29
Ethanol	C ₂ H ₅ OH	0.2	-4.65	-1.82	0.03
Ethylene	C ₂ H ₄	0.136	5.58	-3.0	0.63
Helium	He	5.193	0	0	0
Hydrogen	H ₂	13.46	4.6	-6.85	3.79
Methane	CH ₄	1.2	3.25	0.75	-0.71
Methanol	CH ₃ OH	0.66	2.21	0.81	-0.89
Neon	Ne	1.03	0	0	0
Nitric oxide	NO	0.98	-0.031	0.325	-0.14
Nitrogen	N ₂	1.11	-0.48	0.96	-0.42
Nitrous oxide	N ₂ O	0.49	1.65	-1.31	0.42
n-Octane	C ₈ H ₁₈	-0.053	6.75	-3.67	0.775
Oxygen	O ₂	0.88	-0.0001	0.54	-0.33
Propane	C ₃ H ₈	-0.096	6.95	-3.6	0.73
R-12*	CCl ₂ F ₂	0.26	1.47	-1.25	0.36
R-22*	CHClF ₂	0.2	1.87	-1.35	0.35
R-32*	CF ₂ H ₂	0.227	2.27	-0.93	0.041
R-125*	CHF ₂ CF ₃	0.305	1.68	-0.284	0
R-134a*	CF ₃ CH ₂ F	0.165	2.81	-2.23	1.11
Sulfur dioxide	SO ₂	0.37	1.05	-0.77	0.21
Sulfur trioxide	SO ₃	0.24	1.7	-1.5	0.46

EX.2 Calculate the change in entropy per kilogram as air is heated from 300 to 600 K while pressure drops from 400 to 300 kPa. Assume:

1. Constant specific heat.
2. Variable specific heat

Solution

1. From Table A.5 for air at 300 K,

$$C_{p0} = 1.004 \text{ kJ/kg K}$$

$$s_2 - s_1 = 1.004 \ln \left(\frac{600}{300} \right) - 0.287 \ln \left(\frac{300}{400} \right) = 0.7785 \text{ kJ/kg K}$$

2. From Table A.7,

$$s_{T1}^0 = 6.8693 \text{ kJ/kg K},$$

$$s_{T2}^0 = 7.5764 \text{ kJ/kg K}$$

$$s_2 - s_1 = 7.5764 - 6.8693 - 0.287 \ln \left(\frac{300}{400} \right) = 0.7897 \text{ kJ/kg K}$$

ENTROPY GENERATION

Considerations is that the entropy change in an irreversible process is larger than the change in a reversible process for the same δQ and T . This can be written out in a common form as an equality

$$dS = \frac{\delta Q}{T} + \delta S_{\text{gen}}$$

provided that the last term is positive,

$$\delta S_{\text{gen}} \geq 0$$

The amount of entropy, δS_{gen} , is the entropy generation in the process due to irreversibilities occurring inside the system, a control mass for now but later extended to the more general control volume.

In addition to this internal entropy generation, external irreversibilities are possible by heat transfer over finite temperature differences as the δQ is transferred from a reservoir or by the mechanical transfer of work.

Consider a reversible process, for which the entropy generation is zero, and the heat transfer and work terms therefore are

$$\delta Q = T dS \quad \text{and} \quad \delta W = P dV$$

For an irreversible process with a nonzero entropy generation,

$$\delta Q_{\text{irr}} = T dS - T \delta S_{\text{gen}}$$

and thus is smaller than that for the reversible case for the same change of state, dS . we also note that for the irreversible process, the work is no longer equal to PdV but is smaller. Furthermore, since the first law is

$$\delta Q_{\text{irr}} = dU + \delta W_{\text{irr}}$$

and the property relation is valid,

$$T dS = dU + P dV$$

it is found that

$$\delta W_{\text{irr}} = P dV - T \delta S_{\text{gen}}$$

showing that the work is reduced by an amount proportional to the entropy generation. For this reason the term $T \delta S_{\text{gen}}$ is often called lost work, although it is not a real work or energy quantity lost but rather a lost opportunity to extract work.

It can be integrated between initial and final states to

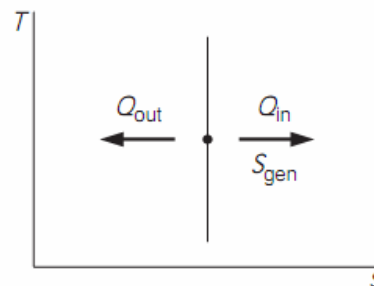
$$S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{\delta Q}{T} + S_{2 \text{ gen}}$$

The entropy balance equation for a control mass in the same form as the energy equation

$$\Delta \text{Entropy} = +\text{in} - \text{out} + \text{gen}$$

Some important conclusions can be as **First**, there are two ways in which the entropy of a system can be increased—by transferring heat to it and by having an irreversible process. Since the entropy generation cannot be less than zero, there is only one way in which the entropy of a system can be decreased, and that is to transfer heat from the system. These changes are illustrated in a T–s diagram in Fig.1 showing the half-plane into which the state moves due to a heat transfer or an entropy generation. **Second**, as we have already noted for an adiabatic process, $\delta Q = 0$, and therefore the increase in entropy is always associated with the irreversibilities. **Third**, the presence of irreversibilities will cause the work to be smaller than the reversible work. This means less work out in an expansion process and more work into the control mass ($\delta W < 0$) in a compression process.

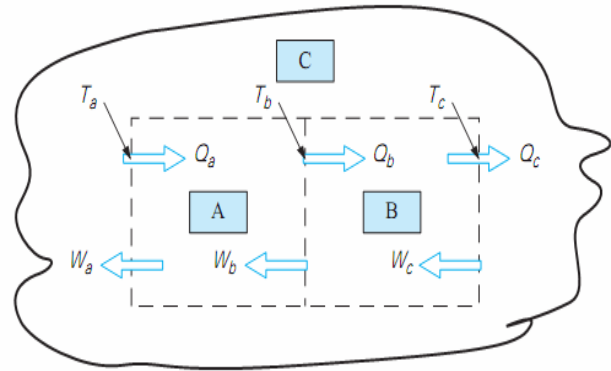
FIG. Change of entropy due to heat transfer and entropy generation



PRINCIPLE OF THE INCREASE OF ENTROPY

The entropy change of a control mass could be either positive or negative, since entropy can be increased by internal entropy generation and either increased or decreased by heat transfer, depending on the direction of that transfer. Consider two mutually exclusive control volumes A and B with a common surface and their surroundings C such that they collectively include the whole world. Let some processes take place so that these control volumes exchange work and heat transfer as indicated in Fig.2. Since a Q or W is transferred from one control volume to another, we only keep one symbol for each term and give the direction with the arrow.

FIG.2 Total
world divided into three
control volumes



$$\text{Change} = +\text{in} - \text{out} + \text{generation}$$

and refer to the figure for the sign. We should know, however, that we cannot generate energy, but only entropy.

Energy:

$$(E_2 - E_1)_A = Q_a - W_a - Q_b + W_b$$

$$(E_2 - E_1)_B = Q_b - W_b - Q_c + W_c$$

$$(E_2 - E_1)_C = Q_c + W_a - Q_a - W_c$$

Entropy:

$$(S_2 - S_1)_A = \int \frac{\delta Q_a}{T_a} - \int \frac{\delta Q_b}{T_b} + S_{\text{gen } A}$$

$$(S_2 - S_1)_B = \int \frac{\delta Q_b}{T_b} - \int \frac{\delta Q_c}{T_c} + S_{\text{gen } B}$$

$$(S_2 - S_1)_C = \int \frac{\delta Q_c}{T_c} - \int \frac{\delta Q_a}{T_a} + S_{\text{gen } C}$$

Now we add all the energy equations to get the energy change for the total world:

$$\begin{aligned} (E_2 - E_1)_{\text{total}} &= (E_2 - E_1)_A + (E_2 - E_1)_B + (E_2 - E_1)_C \\ &= Q_a - W_a - Q_b + W_b + Q_b - W_b - Q_c + W_c + Q_c + W_a - Q_a - W_c \\ &= 0 \end{aligned}$$

The energy is not stored in the same form or place as it was before the process, but the total amount is the same. For entropy we get something slightly different:

$$\begin{aligned}
 (S_2 - S_1)_{\text{total}} &= (S_2 - S_1)_A + (S_2 - S_1)_B + (S_2 - S_1)_C \\
 &= \int \frac{\delta Q_a}{T_a} - \int \frac{\delta Q_b}{T_b} + S_{\text{gen } A} + \int \frac{\delta Q_b}{T_b} - \int \frac{\delta Q_c}{T_c} + S_{\text{gen } B} \\
 &\quad + \int \frac{\delta Q_c}{T_c} - \int \frac{\delta Q_a}{T_a} + S_{\text{gen } C} \\
 &= S_{\text{gen } A} + S_{\text{gen } B} + S_{\text{gen } C} \geq 0
 \end{aligned}$$

As shown in Fig. 3. Let control volume A be a control mass at temperature T that receives a heat transfer of δQ from a surrounding control volume C at uniform temperature T_0 . The transfer goes through the walls, control volume B, that separates domains A and C. Let us then analyze the incremental process from the point of view of control volume B, the walls, which do not have a change of state in time, but the state is nonuniform in space (it has T_0 on the outer side and T on the inner side).

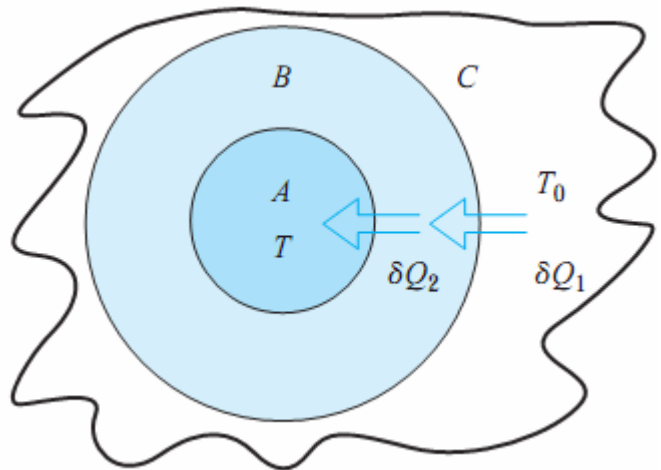
Energy Eq.: $dE = 0 = \delta Q_1 - \delta Q_2 \Rightarrow \delta Q_1 = \delta Q_2 = \delta Q$

Entropy Eq.: $dS = 0 = \frac{\delta Q}{T_0} - \frac{\delta Q}{T} + \delta S_{\text{gen } B}$

So, from the energy equation, we find the two heat transfers to be the same, but realize that they take place at two different temperatures leading to an entropy generation as

$$\delta S_{\text{gen } B} = \frac{\delta Q}{T} - \frac{\delta Q}{T_0} = \delta Q \left(\frac{1}{T} - \frac{1}{T_0} \right) \geq 0$$

FIG.3 Heat transfer through a wall.



EX.1 Suppose that 1 kg of saturated water vapor at 100° C is condensed to a saturated liquid at 100°C in a constant-pressure process by heat transfer to the surrounding air, which is at 25°C. What is the net increase in entropy of the water plus surroundings?

Solution

For the control mass (water), from the steam tables, we obtain

$$\Delta S_{c.m.} = -ms_{fg} = -1 \times 6.0480 = -6.0480 \text{ kJ/K}$$

Concerning the surroundings, we have

$$Q_{\text{to surroundings}} = mh_{fg} = 1 \times 2257.0 = 2257 \text{ kJ}$$

$$\Delta S_{\text{surr}} = \frac{Q}{T_0} = \frac{2257}{298.15} = 7.5700 \text{ kJ/K}$$

$$\Delta S_{\text{gen total}} = \Delta S_{c.m.} + \Delta S_{\text{surr}} = -6.0480 + 7.5700 = 1.5220 \text{ kJ/K}$$

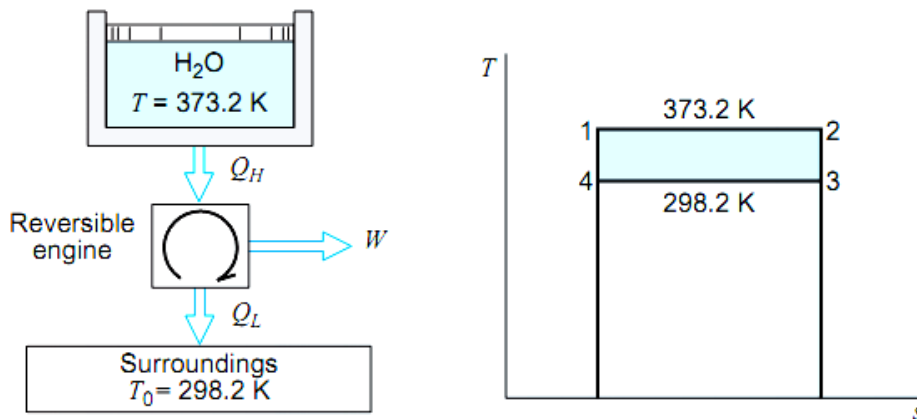
The decrease in the entropy of the water is equal to the increase in the entropy of the surroundings.

$$\Delta S_{c.m.} = -6.0480 \text{ kJ/K}$$

$$\Delta S_{\text{surr}} = 6.0480 \text{ kJ/K}$$

$$Q_{\text{to surroundings}} = T_0 \Delta S = 298.15(6.0480) = 1803.2 \text{ kJ}$$

$$W = Q_H - Q_L = 2257 - 1803.2 = 453.8 \text{ kJ}$$



ENTROPY AS A RATE EQUATION

The second law of thermodynamics was used to write the balance of entropy. The rate form is also the basis for the development of the entropy balance equation in the general control volume analysis for an unsteady situation.

$$\frac{dS}{dt} = \frac{1}{T} \frac{\delta Q}{dt} + \frac{\delta S_{\text{gen}}}{dt}$$

Using this and a dot to indicate a rate, the final form for the entropy equation in the limit is

$$\frac{dS_{\text{c.m.}}}{dt} = \sum \frac{1}{T} \dot{Q} + \dot{S}_{\text{gen}}$$

EX.3 Consider an electric space heater that converts 1 kW of electric power into a heat flux of 1 kW delivered at 600 K from the hot wire surface. Let us look at the process of the energy conversion from electricity to heat transfer and find the rate of total entropy generation.

Analysis

The first and second laws of thermodynamics in rate form become

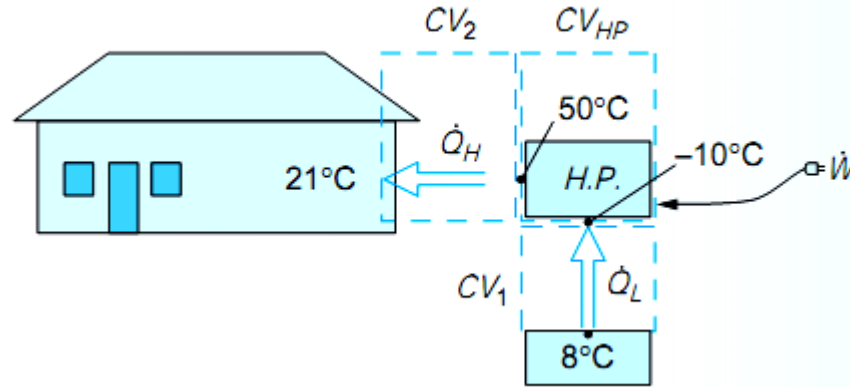
$$\begin{aligned} \frac{dE_{\text{c.m.}}}{dt} &= \frac{dU_{\text{c.m.}}}{dt} = 0 = \dot{W}_{\text{el.in}} - \dot{Q}_{\text{out}} \\ \frac{dS_{\text{c.m.}}}{dt} &= 0 = -\dot{Q}_{\text{out}}/T_{\text{surface}} + \dot{S}_{\text{gen}} \end{aligned}$$

Solution

We now get the entropy generation as

$$\dot{S}_{\text{gen}} = \dot{Q}_{\text{out}}/T = 1 \text{ kW}/600 \text{ K} = 0.00167 \text{ kW/K}$$

EX.4 Consider a modern air conditioner using R-410a working in heat pump mode, as shown in Fig. It has aCOP of 4 with 10 kW of power input. The cold side is buried underground, where it is 8°C, and the hot side is a house kept at 21°C. For simplicity, assume that the cycle has a high temperature of 50°C and a low temperature of -10°C. We would like to know where entropy is generated associated with the heat pump, assuming steady-state operation.



Let us look first at the heat pump itself, as in CV_{HP} , so from the COP

$$\dot{Q}_H = \beta_{HP} \times \dot{W} = 4 \times 10 \text{ kW} = 40 \text{ kW}$$

Energy Eq.: $\dot{Q}_L = \dot{Q}_H - \dot{W} = 40 \text{ kW} - 10 \text{ kW} = 30 \text{ kW}$

Entropy Eq.: $0 = \frac{\dot{Q}_L}{T_{\text{low}}} - \frac{\dot{Q}_H}{T_{\text{high}}} + \dot{S}_{\text{gen}HP}$

$$\dot{S}_{\text{gen}HP} = \frac{\dot{Q}_H}{T_{\text{high}}} - \frac{\dot{Q}_L}{T_{\text{low}}} = \frac{40 \text{ kW}}{323 \text{ K}} - \frac{30 \text{ kW}}{263 \text{ K}} = 9.8 \text{ W/K}$$

Now consider CV_1 from the underground 8°C to the cycle -10°C.

Entropy Eq.: $0 = \frac{\dot{Q}_L}{T_L} - \frac{\dot{Q}_L}{T_{\text{low}}} + \dot{S}_{\text{gen}CV_1}$

$$\dot{S}_{\text{gen}CV_1} = \frac{\dot{Q}_L}{T_{\text{low}}} - \frac{\dot{Q}_L}{T_L} = \frac{30 \text{ kW}}{263 \text{ K}} - \frac{30 \text{ kW}}{281 \text{ K}} = 7.3 \text{ W/K}$$

And finally, consider CV_2 from the heat pump at 50°C to the house at 21°C.

Entropy Eq.: $0 = \frac{\dot{Q}_H}{T_{\text{high}}} - \frac{\dot{Q}_H}{T_H} + \dot{S}_{\text{gen}CV_2}$

$$\dot{S}_{\text{gen}CV_2} = \frac{\dot{Q}_H}{T_H} - \frac{\dot{Q}_H}{T_{\text{high}}} = \frac{40 \text{ kW}}{294 \text{ K}} - \frac{40 \text{ kW}}{323 \text{ K}} = 12.2 \text{ W/K}$$

The total entropy generation rate becomes

$$\begin{aligned}\dot{S}_{\text{genTOT}} &= \dot{S}_{\text{gen}CV_1} + \dot{S}_{\text{gen}CV_2} + \dot{S}_{\text{gen}HP} \\ &= \frac{\dot{Q}_L}{T_{\text{low}}} - \frac{\dot{Q}_L}{T_L} + \frac{\dot{Q}_H}{T_H} - \frac{\dot{Q}_H}{T_{\text{high}}} + \frac{\dot{Q}_H}{T_{\text{high}}} - \frac{\dot{Q}_L}{T_{\text{low}}} \\ &= \frac{\dot{Q}_H}{T_H} - \frac{\dot{Q}_L}{T_L} = \frac{40 \text{ kW}}{294 \text{ K}} - \frac{30 \text{ kW}}{281 \text{ K}} = 29.3 \text{ W/K}\end{aligned}$$

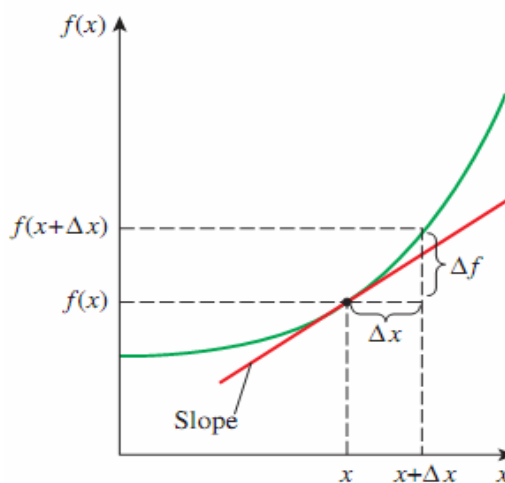
Chapter Three Thermodynamic Relations

A LITTLE MATH—PARTIAL DERIVATIVES AND ASSOCIATED RELATIONS

Consider a function f that depends on a single variable x , that is, $f = f(x)$. Fig.1 shows such a function that starts out flat but gets rather steep as x increases. The steepness of the curve is a measure of the degree of dependence of f on x . In our case, the function f depends on x more strongly at larger x values. The steepness of a curve at a point is measured by the slope of a line tangent to the curve at that point, and it is equivalent to the derivative of the function at that point defined as

FIG.1
The derivative of a function at a specified point represents the slope of the function at that point

$$\frac{df}{dx} = \lim_{\Delta x \rightarrow 0} \frac{\Delta f}{\Delta x} = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}$$



Partial Differentials

Now consider a function that depends on two (or more) variables, such as $z = z(x, y)$. This time the value of z depends on both x and y . It is sometimes desirable to examine the dependence of z on only one of the variables.

This is illustrated in Fig.2. The symbol ∂ represents differential changes, just like the symbol d . They differ in that the symbol d represents the total differential change of a function and reflects the influence of all variables, whereas ∂ represents the partial differential change due to the variation of a single variable.

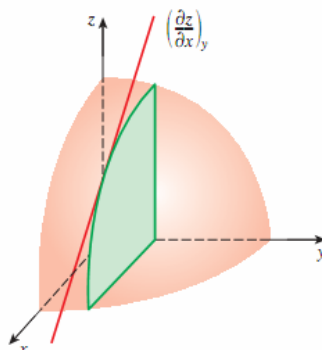
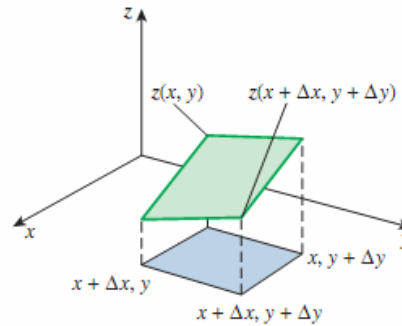


Fig.2
Geometric representation of partial derivative $(\partial z / \partial x)_y$.

To obtain a relation for the total differential change in $z(x, y)$ for simultaneous changes in x and y , consider a small portion of the surface $z(x, y)$ shown in Fig.3. When the independent variables x and y change by Dx and Dy , respectively, the dependent variable z changes by Dz , which can be expressed as:

Fig.3
Geometric representation of total derivative dz for a function $z(x, y)$.



Taking the limits as $Dx \rightarrow 0$ and $Dy \rightarrow 0$ and using the definitions of partial derivatives, we obtain

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

Ex.1 Consider air at 300 K and 0.86 m³/kg. The state of air changes to 302 K and 0.87 m³/kg as a result of some disturbance, estimate the change in the pressure of air?

SOLUTION The temperature and specific volume of air changes slightly during a process. The resulting change in pressure is to be determined.

Assumption Air is an ideal gas.

$$dT \cong \Delta T = (302 - 300) \text{ K} = 2 \text{ K}$$

and

$$dv \cong \Delta v = (0.87 - 0.86) \text{ m}^3/\text{kg} = 0.01 \text{ m}^3/\text{kg}$$

An ideal gas obeys the relation $Pv = RT$. Solving for P yields

$$P = \frac{RT}{v}$$

Note that R is a constant and $P = P(T, v)$. Applying Eq. 12-3 and using average values for T and v ,

$$\begin{aligned} dP &= \left(\frac{\partial P}{\partial T} \right)_v dT + \left(\frac{\partial P}{\partial v} \right)_T dv = \frac{R dT}{v} - \frac{RT dv}{v^2} \\ &= (0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}) \left[\frac{2 \text{ K}}{0.865 \text{ m}^3/\text{kg}} - \frac{(301 \text{ K})(0.01 \text{ m}^3/\text{kg})}{(0.865 \text{ m}^3/\text{kg})^2} \right] \\ &= 0.664 \text{ kPa} - 1.155 \text{ kPa} \\ &= \mathbf{-0.491 \text{ kPa}} \end{aligned}$$

Partial Differential Relations

Now let us rewrite:-

$$dz = M dx + N dy$$

where

$$M = \left(\frac{\partial z}{\partial x} \right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y} \right)_x$$

Taking the partial derivative of M with respect to y and of N with respect to x yields

$$\left(\frac{\partial M}{\partial y} \right)_x = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x} \right)_y = \frac{\partial^2 z}{\partial y \partial x}$$

The order of differentiation is immaterial for properties since they are continuous point functions and have exact differentials. Therefore, the two relations above are identical:

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

1- THE MAXWELL RELATIONS

The equations that relate the partial derivatives of properties P , v , T , and s of a simple compressible system to each other are called the Maxwell relations. They are obtained from the four Gibbs equations by exploiting the exactness of the differentials of thermodynamic properties.

Two of the Gibbs relations:-

$$du = T ds - P dv$$

$$dh = T ds + v dP$$

The other two Gibbs relations are based on two new combination properties the Helmholtz function a and the Gibbs function g , defined :-

$$a = u - Ts$$

$$g = h - Ts$$

Differentiating, we get

$$da = du - T ds - s dT$$

$$dg = dh - T ds - s dT$$

we obtain the other two Gibbs relations for simple compressible systems:

$$da = -s dT - P dv$$

$$dg = -s dT + v dP$$

A careful examination of the four Gibbs relations reveals that they are of the form

$$dz = M dx + N dy$$

with

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad *$$

since u, h, a, and g are properties and thus have exact differentials. Applying Eq. * to each of them, we obtain

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

These are called the Maxwell relations. They are extremely valuable in thermodynamics because they provide a means of determining the change in entropy, which cannot be measured directly, by simply measuring the changes in properties P, v, and T. Note that the Maxwell relations given above are limited to simple compressible systems.

Ex1 Verify the validity of the last Maxwell relation Eq. $\left(\frac{\partial s}{\partial P}\right)_T \stackrel{?}{=} -\left(\frac{\partial v}{\partial T}\right)_P$ for steam at 250 C and 300 kPa.

$$\left(\frac{\partial s}{\partial P}\right)_T \stackrel{?}{=} -\left(\frac{\partial v}{\partial T}\right)_P$$

$$\left(\frac{\Delta s}{\Delta P}\right)_{T=250^\circ\text{C}} \stackrel{?}{\cong} -\left(\frac{\Delta v}{\Delta T}\right)_{P=300\text{ kPa}}$$

From Super heated steam

$$\left[\frac{s_{400\text{ kPa}} - s_{200\text{ kPa}}}{(400 - 200)\text{ kPa}}\right]_{T=250^\circ\text{C}} \stackrel{?}{\cong} -\left[\frac{v_{300^\circ\text{C}} - v_{200^\circ\text{C}}}{(300 - 200)^\circ\text{C}}\right]_{P=300\text{ kPa}}$$

$$\frac{(7.3804 - 7.7100)\text{ kJ/kg}\cdot\text{K}}{(400 - 200)\text{ kPa}} \stackrel{?}{\cong} -\frac{(0.87535 - 0.71643)\text{ m}^3/\text{kg}}{(300 - 200)^\circ\text{C}}$$

$$-0.00165\text{ m}^3/\text{kg}\cdot\text{K} \cong -0.00159\text{ m}^3/\text{kg}\cdot\text{K}$$

2- THE CLAPEYRON EQUATION

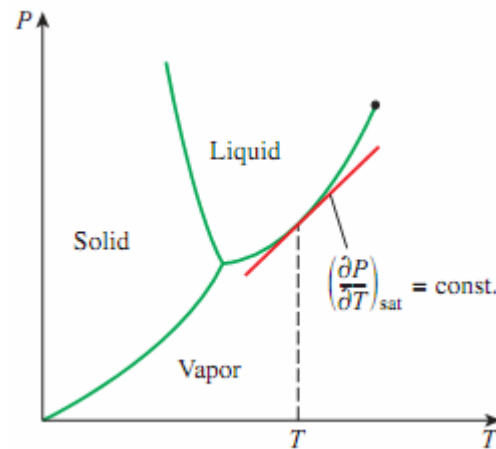
The Maxwell relations have far-reaching implications in thermodynamics and are frequently used to derive useful thermodynamic relations. The Clapeyron equation is one such relation, and it enables us to determine the enthalpy change associated with a phase change (such as the enthalpy of vaporization h_{fg}) from a knowledge of P , v , and T data alone.

Consider the third Maxwell relation $\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$

During a phase-change process, the pressure is the saturation pressure, which depends on the temperature only and is independent of the specific volume. That is, $P_{\text{sat}} = f(T_{\text{sat}})$. Therefore, the partial derivative $(\partial P/\partial T)_v$ can be expressed as a total derivative $(dP/dT)_{\text{sat}}$, which is the slope of the saturation curve on a P - T diagram at a specified saturation state (Fig.4).

FIG.4

The slope of the saturation curve on a P - T diagram is constant at a constant T or P .



For an isothermal liquid–vapor phase-change process, for example, the integration yields

$$s_g - s_f = \left(\frac{dP}{dT}\right)_{\text{sat}} (v_g - v_f)$$

or

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{s_{fg}}{v_{fg}}$$

During this process the pressure also remains constant.

$$dh = T ds + v dP \xrightarrow{0} \int_f^g dh = \int_f^g T ds \rightarrow h_{fg} = T s_{fg}$$

Substituting this result,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T v_{fg}}$$

which is called the Clapeyron equation after the French engineer and physicist E. Clapeyron (1799–1864). This is an important thermodynamic relation since it enables us to determine the enthalpy of vaporization h_{fg} at a given temperature by simply measuring the slope of the saturation curve on a P - T diagram and the specific volume of saturated liquid and saturated vapor at the given temperature.

The Clapeyron equation is applicable to any phase-change process that occurs at constant temperature and pressure. It can be expressed in a general form as

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{12}}{T v_{12}}$$

where the subscripts 1 and 2 indicate the two phases.

Ex.2 Using the Clapeyron equation, estimate the value of the enthalpy of vaporization of refrigerant-134a at 20 °C, and compare it with the tabulated value.

SOLUTION The h_{fg} of refrigerant-134a is to be determined using the Clapeyron equation.

$$h_{fg} = T v_{fg} \left(\frac{dP}{dT}\right)_{\text{sat}}$$

where, from Table A-11,

$$\begin{aligned} v_{fg} &= (v_g - v_f)_{@ 20^\circ\text{C}} = 0.036012 - 0.0008160 = 0.035196 \text{ m}^3/\text{kg} \\ \left(\frac{dP}{dT}\right)_{\text{sat}, 20^\circ\text{C}} &\cong \left(\frac{\Delta P}{\Delta T}\right)_{\text{sat}, 20^\circ\text{C}} = \frac{P_{\text{sat @ } 24^\circ\text{C}} - P_{\text{sat @ } 16^\circ\text{C}}}{24^\circ\text{C} - 16^\circ\text{C}} \\ &= \frac{646.18 - 504.58 \text{ kPa}}{8^\circ\text{C}} = 17.70 \text{ kPa/K} \end{aligned}$$

since $\Delta T(^{\circ}\text{C}) \equiv \Delta T(\text{K})$. Substituting, we get

$$\begin{aligned} h_{fg} &= (293.15 \text{ K})(0.035196 \text{ m}^3/\text{kg})(17.70 \text{ kPa/K}) \left(\frac{1 \text{ kJ}}{1 \text{ kPa}\cdot\text{m}^3}\right) \\ &= 182.62 \text{ kJ/kg} \end{aligned}$$

The Clapeyron equation can be simplified for liquid–vapor and solid–vapor phase changes by utilizing some approximations. At low pressures $v_g \gg v_f$, and thus $v_{fg} = v_g$. By treating the vapor as an ideal gas, we have $v_g = RT/P$.

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{Ph_{fg}}{RT^2}$$

or

$$\left(\frac{dP}{P}\right)_{\text{sat}} = \frac{h_{fg}}{R} \left(\frac{dT}{T^2}\right)_{\text{sat}}$$

For small temperature intervals h_{fg} can be treated as a constant at some average value. Then integrating this equation between two saturation states yields

$$\ln\left(\frac{P_2}{P_1}\right)_{\text{sat}} \cong \frac{h_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{\text{sat}}$$

This equation is called the Clapeyron–Clausius equation, and it can be used to determine the variation of saturation pressure with temperature. It can also be used in the solid–vapor region by replacing h_{fg} by h_{ig} (the enthalpy of sublimation) of the substance.

Ex.3 Estimate the saturation pressure of refrigerant-134a at -50 F, using the data available in the refrigerant tables.

SOLUTION The saturation pressure of refrigerant-134a is to be determined using other tabulated data.

Analysis Table A–11E lists saturation data at temperatures -40 F and above. Therefore, we should either resort to other sources or use extrapolation to obtain saturation data at lower temperatures, provides an intelligent way to extrapolate:

$$\ln\left(\frac{P_2}{P_1}\right)_{\text{sat}} \cong \frac{h_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{\text{sat}}$$

In our case $T_1 = -40^\circ\text{F}$ and $T_2 = -50^\circ\text{F}$. For refrigerant-134a, $R = 0.01946$ Btu/lbm·R. Also from Table A–11E at -40°F , we read $h_{fg} = 97.104$ Btu/lbm and $P_1 = P_{\text{sat @ } -40^\circ\text{F}} = 7.432$ psia. Substituting these values into gives

$$\ln\left(\frac{P_2}{7.432 \text{ psia}}\right) \cong \frac{97.104 \text{ Btu/lbm}}{0.01946 \text{ Btu/lbm}\cdot\text{R}} \left(\frac{1}{420 \text{ R}} - \frac{1}{410 \text{ R}}\right)$$

$$P_2 \cong 5.56 \text{ psia}$$

GENERAL RELATIONS FOR du , dh , ds , C_v , AND C_p

Internal Energy Changes

We choose the internal energy to be a function of T and v ; that is, $u = u(T, v)$ and take its total differential

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

Using the definition of c_v , we have

$$du = c_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

Now we choose the entropy to be a function of T and v ; that is, $s = s(T, v)$ and take its total differential,

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv$$

Substituting this into the $T ds$ relation $du = T ds - P dv$ yields

$$du = T \left(\frac{\partial s}{\partial T} \right)_v dT + \left[T \left(\frac{\partial s}{\partial v} \right)_T - P \right] dv$$

Equating the coefficients of dT and dv in

$$\begin{aligned} \left(\frac{\partial s}{\partial T} \right)_v &= \frac{c_v}{T} \\ \left(\frac{\partial u}{\partial v} \right)_T &= T \left(\frac{\partial s}{\partial v} \right)_T - P \end{aligned}$$

Using the third Maxwell relation

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_v - P$$

Substituting this into Eq.

$$du = c_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$$

The change in internal energy of a simple compressible system associated with a change of state from (T_1, v_1) to (T_2, v_2) is determined by integration:

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v dT + \int_{v_1}^{v_2} \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$$

Enthalpy Changes

The general relation for dh is determined in exactly the same manner. This time we choose the enthalpy to be a function of T and P , that is, $h = h(T, P)$, and take its total differential:-

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP$$

Using the definition of c_p , we have

$$dh = c_p dT + \left(\frac{\partial h}{\partial P} \right)_T dP$$

Now we choose the entropy to be a function of T and P ; that is, we take $s = s(T, P)$ and take its total differential,

$$ds = \left(\frac{\partial s}{\partial T} \right)_P dT + \left(\frac{\partial s}{\partial P} \right)_T dP$$

Substituting this into the $T ds$ relation $dh = T ds + v dP$ gives

$$dh = T \left(\frac{\partial s}{\partial T} \right)_P dT + \left[v + T \left(\frac{\partial s}{\partial P} \right)_T \right] dP$$

Equating the coefficients of dT and dP in Eqs.

$$\begin{aligned} \left(\frac{\partial s}{\partial T} \right)_P &= \frac{c_p}{T} \\ \left(\frac{\partial h}{\partial P} \right)_T &= v + T \left(\frac{\partial s}{\partial P} \right)_T \end{aligned}$$

Using the fourth Maxwell relation

$$\left(\frac{\partial h}{\partial P} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_P$$

Substituting this into Eq.

$$dh = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

The change in enthalpy of a simple compressible system associated with a change of state from (T_1, P_1) to (T_2, P_2) is determined by integration:

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

In reality, one needs only to determine either $(u_2 - u_1)$ from $(h_2 - h_1)$, depending on which is more suitable to the data at hand. The other can easily be determined by using the definition of enthalpy $h = u + Pv$:-

$$h_2 - h_1 = u_2 - u_1 + (P_2 v_2 - P_1 v_1)$$

Entropy Changes

Below we develop two general relations for the entropy change of a simple compressible system. The first relation is obtained by replacing the first partial derivative in the total differential ds

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv$$

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial s}{\partial v} \right)_T - P$$

the second partial derivative by the third Maxwell relation

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_v$$

yielding:-

$$ds = \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_v dv$$

and

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v}{T} dT + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T} \right)_v dv$$

The second relation is obtained by replacing the first partial derivative in the total differential of ds

$$ds = \left(\frac{\partial s}{\partial T} \right)_P dT + \left(\frac{\partial s}{\partial P} \right)_T dP$$

$$\left(\frac{\partial h}{\partial P} \right)_T = v + T \left(\frac{\partial s}{\partial P} \right)_T$$

and the second partial derivative by the fourth Maxwell relation

$$\left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P$$

yielding

$$ds = \frac{c_P}{T} dT - \left(\frac{\partial v}{\partial T} \right)_P dP$$

and

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_P}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T} \right)_P dP$$

EXERGY

The second law of thermodynamics has proved to be a very powerful tool in the optimization of complex thermodynamic systems. We examine the performance of engineering devices in light of the second law of thermodynamics. It is start our discussions with the introduction of exergy (also called availability), which is the maximum useful work that could be obtained from the system at a given state in a specified environment, and to continue with the reversible work, which is the maximum useful work that can be obtained as a system undergoes a process between two specified states. Next we discuss the irreversibility (also called the exergy destruction or lost work), which is the wasted work potential during a process as a result of irreversibilities, and we define a second-law efficiency. We then develop the exergy balance relation and apply it to closed systems and control volumes.

Exergy (Work Potential) Associated with Kinetic and Potential Energy

Kinetic energy is a form of mechanical energy, and thus it can be converted to work entirely. Therefore, the work potential or exergy of the kinetic energy of a system is equal to the kinetic energy itself regardless of the temperature and pressure of the environment. That is,

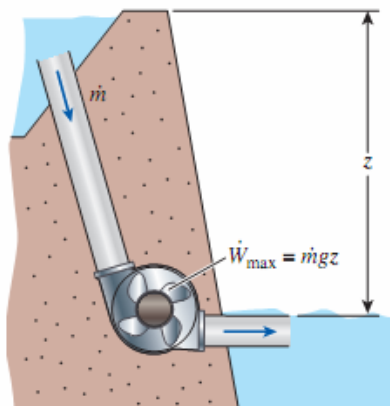
$$\text{Exergy of kinetic energy: } x_{ke} = ke = \frac{V^2}{2} \quad (\text{kJ/kg})$$

Potential energy is also a form of mechanical energy, and thus it can be converted to work entirely. Therefore, the exergy of the potential energy of a system is equal to the potential energy itself regardless of the temperature and pressure of the environment (Fig. 1). That is,

$$\text{Exergy of potential energy: } x_{pe} = pe = gz \quad (\text{kJ/kg})$$

FIGURE 1

The work potential or exergy of potential energy is equal to the potential energy itself.



Ex.1 A wind turbine with a 12-m-diameter rotor, as shown in Fig. , is to be installed at a location where the wind is blowing steadily at an average velocity of 10 m/s. Determine the maximum power that can be generated by the wind turbine?

Assumptions Air is at standard conditions of 1 atm and 25°C, and thus its density is 1.18 kg/m³.

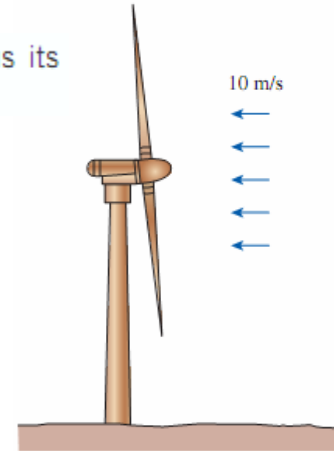
Therefore, the exergy of the blowing air is simply the kinetic energy it possesses:

$$ke = \frac{V^2}{2} = \frac{(10 \text{ m/s})^2}{2} \left(\frac{1 \text{ kJ/kg}}{1000 \text{ m}^2/\text{s}^2} \right) = 0.05 \text{ kJ/kg}$$

$$\dot{m} = \rho AV = \rho \frac{\pi D^2}{4} V = (1.18 \text{ kg/m}^3) \frac{\pi (12 \text{ m})^2}{4} (10 \text{ m/s}) = 1335 \text{ kg/s}$$

Thus,

$$\text{Maximum power} = \dot{m}(ke) = (1335 \text{ kg/s})(0.05 \text{ kJ/kg}) = \mathbf{66.8 \text{ kW}}$$



Ex.2 Consider a large furnace that can transfer heat at a temperature of 2000 R at a steady rate of 3000 Btu/s. Determine the rate of exergy flow associated with this heat transfer. Assume an environment temperature of 77 F.

The thermal efficiency of this reversible heat engine is

$$\eta_{th,max} = \eta_{th,rev} = 1 - \frac{T_L}{T_H} = 1 - \frac{T_0}{T_H} = 1 - \frac{537 \text{ R}}{2000 \text{ R}} = 0.732 \text{ (or 73.2\%)}$$

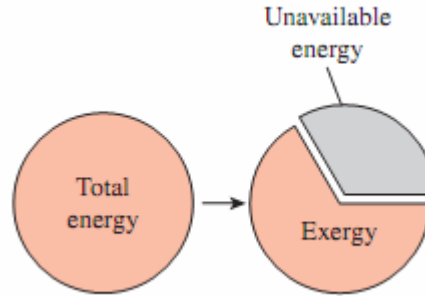
That is, a heat engine can convert, at best, 73.2 percent of the heat received from this furnace to work. Thus, the exergy of this furnace is equivalent to the power produced by the reversible heat engine:

$$\dot{W}_{max} = \dot{W}_{rev} = \eta_{th,rev} \dot{Q}_{in} = (0.732)(3000 \text{ Btu/s}) = \mathbf{2196 \text{ Btu/s}}$$

Notice that 26.8 (1- 0.732) percent of the heat transferred from the furnace is not available for doing work. The portion of energy that cannot be converted to work is called unavailable energy (Fig. 2). Unavailable energy is simply the difference between the total energy of a system at a specified state and the exergy of that energy.

FIGURE.2

Unavailable energy is the portion of energy that cannot be converted to work by even a reversible heat engine.



REVERSIBLE WORK AND IRREVERSIBILITY

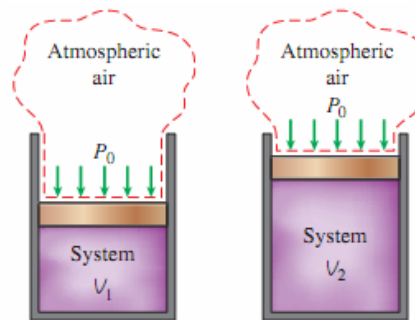
These two quantities are the reversible work and irreversibility (or exergy destruction). But first we examine the surroundings work, which is the work done by or against the surroundings during a process.

The work done by work-producing devices is not always entirely in a usable form. For example, when a gas in a piston–cylinder device expands, part of the work done by the gas is used to push the atmospheric air out of the way of the piston (Fig. 3). This work, which cannot be recovered and utilized for any useful purpose, is equal to the atmospheric pressure P_0 times the volume change of the system,

$$W_{\text{surr}} = P_0(V_2 - V_1)$$

FIGURE.3

As a closed system expands, some work needs to be done to push the atmospheric air out of the way (W_{surr}).



The difference between the actual work W and the surroundings work W_{surr} is called the useful work W_u :

$$W_u = W - W_{\text{surr}} = W - P_0(V_2 - V_1)$$

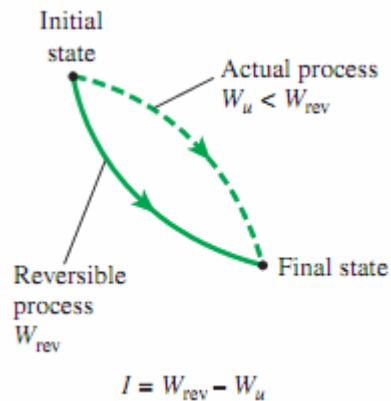
Reversible work W_{rev} is defined as the maximum amount of useful work that can be produced (or the minimum work that needs to be supplied) as a system undergoes a process between the specified initial and final states. This is the useful work output (or input) obtained (or expended) when the process between the initial and final states is executed in a totally reversible manner.

Any difference between the reversible work W_{rev} and the useful work W_u is due to the irreversibilities present during the process, and this difference is called irreversibility I . It is expressed as (Fig. 4)

$$I = W_{\text{rev,out}} - W_{u,\text{out}} \quad \text{or} \quad I = W_{u,\text{in}} - W_{\text{rev,in}}$$

FIGURE 4

The difference between reversible work and actual useful work is the irreversibility.

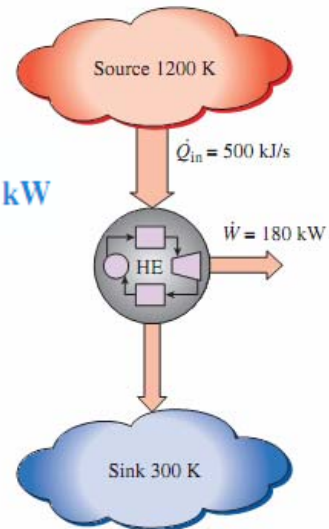


Ex.3 A heat engine receives heat from a source at 1200 K at a rate of 500 kJ/s and rejects the waste heat to a medium at 300 K (Fig.). The power output of the heat engine is 180 kW. Determine the reversible power and the irreversibility rate for this process.
Ans.

$$\dot{W}_{\text{rev,out}} = \eta_{\text{th,rev}} \dot{Q}_{\text{in}} = \left(1 - \frac{T_{\text{sink}}}{T_{\text{source}}}\right) \dot{Q}_{\text{in}} = \left(1 - \frac{300 \text{ K}}{1200 \text{ K}}\right) (500 \text{ kW}) = 375 \text{ kW}$$

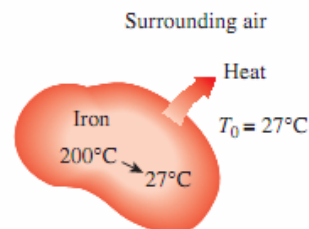
The irreversibility rate is the difference between the reversible power (maximum power that could have been produced) and the useful power output:

$$\dot{I} = \dot{W}_{\text{rev,out}} - \dot{W}_{u,\text{out}} = 375 - 180 = 195 \text{ kW}$$



Ex.4 A 500-kg iron block shown in Fig. is initially at 200 C and is allowed to cool to 27 C by transferring heat to the surrounding air at 27 C. Determine the reversible work and the irreversibility for this process.

Ans.



The reversible work in this case is determined by considering a series of imaginary reversible heat engines operating between the source (at a variable temperature T) and the sink (at a constant temperature T_0), as shown in Fig. Summing their work output:

$$\delta W_{\text{rev}} = \eta_{\text{th,rev}} \delta Q_{\text{in}} = \left(1 - \frac{T_{\text{sink}}}{T_{\text{source}}}\right) \delta Q_{\text{in}} = \left(1 - \frac{T_0}{T}\right) \delta Q_{\text{in}}$$

and

$$W_{\text{rev}} = \int \left(1 - \frac{T_0}{T}\right) \delta Q_{\text{in}}$$

The source temperature T changes from $T_1 = 200^\circ\text{C} = 473\text{ K}$ to $T_0 = 27^\circ\text{C} = 300\text{ K}$ during this process.

A relation for the differential heat transfer from the iron block can be obtained from the differential form of the energy balance applied on the iron block,

$$\underbrace{\delta E_{\text{in}} - \delta E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{dE_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}}$$

$$-\delta Q_{\text{out}} = dU = mc_{\text{avg}}dT$$

Then,

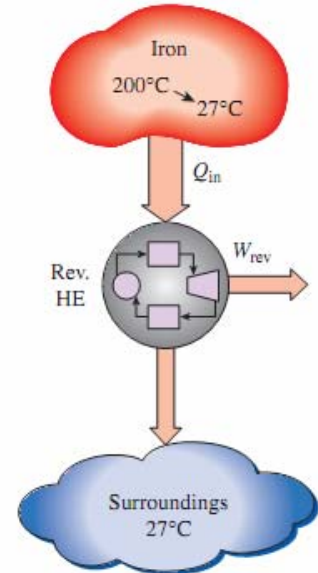
$$\delta Q_{\text{in,heat engine}} = \delta Q_{\text{out,system}} = -mc_{\text{avg}}dT$$

Since heat transfers from the iron and to the heat engine are equal in magnitude and opposite in direction. Substituting and performing the integration, the reversible work is determined to be

$$\begin{aligned} W_{\text{rev}} &= \int_{T_1}^{T_0} \left(1 - \frac{T_0}{T}\right) (-mc_{\text{avg}} dT) = mc_{\text{avg}}(T_1 - T_0) - mc_{\text{avg}} T_0 \ln \frac{T_1}{T_0} \\ &= (500\text{ kg})(0.45\text{ kJ/kg}\cdot\text{K}) \left[(473 - 300)\text{ K} - (300\text{ K}) \ln \frac{473\text{ K}}{300\text{ K}} \right] \\ &= \mathbf{8191\text{ kJ}} \end{aligned}$$

The irreversibility for this process is determined from its definition,

$$I = W_{\text{rev}} - W_u = 8191 - 0 = \mathbf{8191\text{ kJ}}$$



GAS MIXTURES

1 - COMPOSITION OF A GAS MIXTURE: MASS AND MOLE FRACTIONS

To determine the properties of a mixture, we need to know the composition of the mixture as well as the properties of the individual components. There are two ways to describe the composition of a mixture: either by specifying the number of moles of each component, called molar analysis, or by specifying the mass of each component, called gravimetric analysis. Consider a gas mixture composed of k components. The mass of the mixture m_m is the sum of the masses of the individual components, and the mole number of the mixture N_m is the sum of the mole numbers of the individual components (Figs. 1 and 2). That is

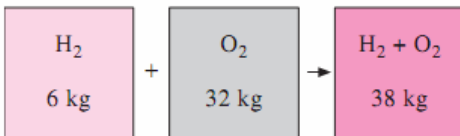


Fig 1 The mass of a mixture is equal to the sum of the masses of its components

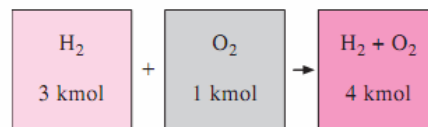


Fig2 The number of moles of a nonreacting mixture is equal to the sum of the number of moles of its components.

$$m_m = \sum_{i=1}^k m_i \quad \text{and} \quad N_m = \sum_{i=1}^k N_i \quad 1$$

The ratio of the mass of a component to the mass of the mixture is called the mass fraction mf , and the ratio of the mole number of a component to the mole number of the mixture is called the mole fraction y

$$mf_i = \frac{m_i}{m_m} \quad \text{and} \quad y_i = \frac{N_i}{N_m} \quad 2$$

we can easily show that the sum of the mass fractions or mole fractions for a mixture is equal to 1 (Fig-3)

$$\sum_{i=1}^k mf_i = 1 \quad \text{and} \quad \sum_{i=1}^k y_i = 1$$

H ₂ + O ₂
$y_{H_2} = 0.75$
$y_{O_2} = 0.25$
1.00

Fig 3 The sum of the mole fractions of a mixture is equal to 1.

The mass of a substance can be expressed in terms of the mole number N and molar mass M of the substance as $m = NM$. Then the apparent (or average) molar mass and the gas constant of a mixture can be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^k y_i M_i \quad \text{and} \quad R_m = \frac{R_u}{M_m}$$

The molar mass of a mixture can also be expressed as

$$M_m = \frac{m_m}{N_m} = \frac{m_m}{\sum m_i/M_i} = \frac{1}{\sum m_i/(m_m M_i)} = \frac{1}{\sum_{i=1}^k \frac{mf_i}{M_i}}$$

Mass and mole fractions of a mixture are related by

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

Ex.1/ Consider a gas mixture that consists of 3 kg of O₂, 5 kg of N₂, and 12 kg of CH₄, as shown in Fig. below. Determine (a) the mass fraction of each component, (b) the mole fraction of each component, and (c) the average molar mass and gas constant of the mixture?

Ans. (a) The total mass of the mixture is

$$m_m = m_{O_2} + m_{N_2} + m_{CH_4} = 3 + 5 + 12 = 20 \text{ kg}$$

Then the mass fraction of each component becomes

$$mf_{O_2} = \frac{m_{O_2}}{m_m} = \frac{3 \text{ kg}}{20 \text{ kg}} = 0.15$$

$$mf_{N_2} = \frac{m_{N_2}}{m_m} = \frac{5 \text{ kg}}{20 \text{ kg}} = 0.25$$

$$mf_{CH_4} = \frac{m_{CH_4}}{m_m} = \frac{12 \text{ kg}}{20 \text{ kg}} = 0.60$$

(b) To find the mole fractions, we need to determine the mole numbers of each component first:

$$N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{3 \text{ kg}}{32 \text{ kg/kmol}} = 0.094 \text{ kmol}$$

$$N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{5 \text{ kg}}{28 \text{ kg/kmol}} = 0.179 \text{ kmol}$$

$$N_{CH_4} = \frac{m_{CH_4}}{M_{CH_4}} = \frac{12 \text{ kg}}{16 \text{ kg/kmol}} = 0.750 \text{ kmol}$$

Thus,

$$N_m = N_{O_2} + N_{N_2} + N_{CH_4} = 0.094 + 0.179 + 0.750 = 1.023 \text{ kmol}$$

and

$$y_{O_2} = \frac{N_{O_2}}{N_m} = \frac{0.094 \text{ kmol}}{1.023 \text{ kmol}} = 0.092$$

$$y_{N_2} = \frac{N_{N_2}}{N_m} = \frac{0.179 \text{ kmol}}{1.023 \text{ kmol}} = 0.175$$

$$y_{CH_4} = \frac{N_{CH_4}}{N_m} = \frac{0.750 \text{ kmol}}{1.023 \text{ kmol}} = 0.733$$

(c) The average molar mass and gas constant of the mixture are determined from their definitions,

$$M_m = \frac{m_m}{N_m} = \frac{20 \text{ kg}}{1.023 \text{ kmol}} = 19.6 \text{ kg/kmol}$$

or

$$\begin{aligned}
 M_m &= \sum y_i M_i = y_{O_2} M_{O_2} + y_{N_2} M_{N_2} + y_{CH_4} M_{CH_4} \\
 &= (0.092)(32) + (0.175)(28) + (0.733)(16) \\
 &= 19.6 \text{ kg/kmol}
 \end{aligned}$$

Also,

$$R_m = \frac{R_u}{M_m} = \frac{8.314 \text{ kJ}/(\text{kmol} \cdot \text{K})}{19.6 \text{ kg/kmol}} = 0.424 \text{ kJ/kg} \cdot \text{K}$$

2 - P-v-T BEHAVIOR OF GAS MIXTURES: IDEAL AND REAL GASES

An ideal gas is defined as a gas whose molecules are spaced far apart so that the behavior of a molecule is not influenced by the presence of other molecules—a situation encountered at low densities and that real gases approximate this behavior closely when they are at a low pressure or high temperature relative to their critical-point values. The P - v - T behavior of an ideal gas is expressed by the simple relation $Pv = RT$, which is called the ideal-gas equation of state. The P - v - T behavior of real gases is expressed by more complex equations of state or by $Pv = ZRT$, where Z is the compressibility factor. **Dalton's law of additive pressures:** The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume (Fig. 4).

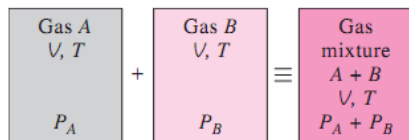


Fig. 4 Dalton's law of additive pressures for a mixture of two ideal gases.

Amagat's law of additive volumes: The volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure (Fig.5).

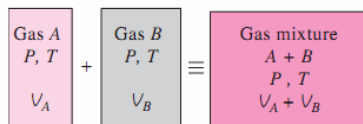


Fig.5 Amagat's law of additive volumes for a mixture of two ideal gases.

Dalton's and Amagat's laws can be expressed as follows:

$$\left. \begin{aligned}
 \text{Dalton's law:} \quad P_m &= \sum_{i=1}^k P_i(T_m, V_m) \\
 \text{Amagat's law:} \quad V_m &= \sum_{i=1}^k V_i(T_m, P_m)
 \end{aligned} \right\} \begin{array}{l} \text{exact for ideal gases,} \\ \text{approximate} \\ \text{for real gases} \end{array}$$

In these relations, P_i is called the component pressure and V_i is called the component volume (Fig.6). Therefore, the volume of each component is equal to the volume of the vessel.) Also, the ratio P_i/P_m is called the pressure fraction and the ratio V_i/V_m is called the volume fraction of component i .



Fig.6 The volume a component would occupy if it existed alone at the mixture T and P is called the component volume (for ideal gases, it is equal to the partial volume $y_i V_m$).

Ideal-Gas Mixtures

For ideal gases, P_i and V_i can be related to y_i by using the ideal-gas relation for both the components and the gas mixture

$$\frac{P_i(T_m, V_m)}{P_m} = \frac{N_i R_u T_m / V_m}{N_m R_u T_m / V_m} = \frac{N_i}{N_m} = y_i$$

$$\frac{V_i(T_m, P_m)}{V_m} = \frac{N_i R_u T_m / P_m}{N_m R_u T_m / P_m} = \frac{N_i}{N_m} = y_i$$

Therefore,

$$\frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

The quantity $y_i P_m$ is called the partial pressure (identical to the component pressure for ideal gases), and the quantity $y_i V_m$ is called the partial volume (identical to the component volume for ideal gases).

Real-Gas Mixtures

Dalton's law of additive pressures and Amagat's law of additive volumes can also be used for real gases, often with reasonable accuracy. This time, however, the component pressures or component volumes should be evaluated from relations:-

$$PV = ZNR_u T$$

The compressibility factor of the mixture Z_m can be expressed in terms of the compressibility factors of the individual gases Z_i by both sides of Dalton's law or Amagat's law expression and simplifying.

$$Z_m = \sum_{i=1}^k y_i Z_i$$

where Z_i is determined either at T_m and V_m (Dalton's law) or at T_m and P_m (Amagat's law) for each individual gas.

Another approach for predicting the P-v-T behavior of a gas mixture is to treat the gas mixture as a pseudopure substance. One such method, proposed by called **Kay's rule**, involves the use of a pseudocritical pressure $P'_{cr,m}$ and pseudocritical temperature $T'_{cr,m}$ for the mixture, defined in terms of the critical pressures and temperatures of the mixture components as

$$P'_{cr,m} = \sum_{i=1}^k y_i P_{cr,i} \quad \text{and} \quad T'_{cr,m} = \sum_{i=1}^k y_i T_{cr,i}$$

Ex.2/ A rigid tank contains 2 kmol of N₂ and 6 kmol of CO₂ gases at 300 K and 15 MPa (Fig. 13–10). Estimate the volume of the tank on the basis of (a) the ideal-gas equation of state, (b) Kay's rule, (c) compressibility factors and Amagat's law, and (d) compressibility factors and Dalton's law.

Ans:- (a) When the mixture is assumed to behave as an ideal gas, the volume of the mixture is easily determined from the ideal-gas relation for the mixture

$$V_m = \frac{N_m R_u T_m}{P_m} = \frac{(8 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(300 \text{ K})}{15,000 \text{ kPa}} = 1.330 \text{ m}^3$$

since

$$N_m = N_{N_2} + N_{CO_2} = 2 + 6 = 8 \text{ kmol}$$

(b) To use Kay's rule, we need to determine the pseudocritical temperature and pseudocritical pressure of the mixture by using the critical-point properties of N₂ and CO₂ from Table A-1. However, first we need to determine the mole fraction of each component

$$y_{N_2} = \frac{N_{N_2}}{N_m} = \frac{2 \text{ kmol}}{8 \text{ kmol}} = 0.25 \quad \text{and} \quad y_{CO_2} = \frac{N_{CO_2}}{N_m} = \frac{6 \text{ kmol}}{8 \text{ kmol}} = 0.75$$

$$T'_{cr,m} = \sum y_i T_{cr,i} = y_{N_2} T_{cr,N_2} + y_{CO_2} T_{cr,CO_2}$$

$$= (0.25)(126.2 \text{ K}) + (0.75)(304.2 \text{ K}) = 259.7 \text{ K}$$

$$P'_{cr,m} = \sum y_i P_{cr,i} = y_{N_2} P_{cr,N_2} + y_{CO_2} P_{cr,CO_2}$$

$$= (0.25)(3.39 \text{ MPa}) + (0.75)(7.39 \text{ MPa}) = 6.39 \text{ MPa}$$

Then,

$$\left. \begin{aligned} T_R &= \frac{T_m}{T'_{cr,m}} = \frac{300 \text{ K}}{259.7 \text{ K}} = 1.16 \\ P_R &= \frac{P_m}{P'_{cr,m}} = \frac{15 \text{ MPa}}{6.39 \text{ MPa}} = 2.35 \end{aligned} \right\} Z_m = 0.49$$

Thus,

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = Z_m V_{ideal} = (0.49)(1.330 \text{ m}^3) = \mathbf{0.652 \text{ m}^3}$$

(c) When Amagat's law is used in conjunction with compressibility factors, Z_m is determined. But first we need to determine the Z of each component on the basis of Amagat's law:

$$N_2: \quad \left. \begin{aligned} T_{R,N_2} &= \frac{T_m}{T_{cr,N_2}} = \frac{300 \text{ K}}{126.2 \text{ K}} = 2.38 \\ P_{R,N_2} &= \frac{P_m}{P_{cr,N_2}} = \frac{15 \text{ MPa}}{3.39 \text{ MPa}} = 4.42 \end{aligned} \right\} Z_{N_2} = 1.02$$

$$CO_2: \quad \left. \begin{aligned} T_{R,CO_2} &= \frac{T_m}{T_{cr,CO_2}} = \frac{300 \text{ K}}{304.2 \text{ K}} = 0.99 \\ P_{R,CO_2} &= \frac{P_m}{P_{cr,CO_2}} = \frac{15 \text{ MPa}}{7.39 \text{ MPa}} = 2.03 \end{aligned} \right\} Z_{CO_2} = 0.30$$

$$\text{Mixture:} \quad Z_m = \sum y_i Z_i = y_{N_2} Z_{N_2} + y_{CO_2} Z_{CO_2}$$

$$= (0.25)(1.02) + (0.75)(0.30) = 0.48$$

Thus,

$$V_m = \frac{Z_m N_m R_u T_m}{P_m} = Z_m V_{ideal} = (0.48)(1.330 \text{ m}^3) = \mathbf{0.638 \text{ m}^3}$$

3- PROPERTIES OF GAS MIXTURES: IDEAL AND REAL GASES

Consider a gas mixture that consists of 2 kg of N_2 and 3 kg of CO_2 . Then the total internal energy, enthalpy, and entropy of a gas mixture can be expressed, respectively, as

$$U_m = \sum_{i=1}^k U_i = \sum_{i=1}^k m_i u_i = \sum_{i=1}^k N_i \bar{u}_i \quad (\text{kJ})$$

$$H_m = \sum_{i=1}^k H_i = \sum_{i=1}^k m_i h_i = \sum_{i=1}^k N_i \bar{h}_i \quad (\text{kJ})$$

$$S_m = \sum_{i=1}^k S_i = \sum_{i=1}^k m_i s_i = \sum_{i=1}^k N_i \bar{s}_i \quad (\text{kJ/K})$$

By following a similar logic, the changes in internal energy, enthalpy, and entropy of a gas mixture during a process can be expressed

$$\Delta U_m = \sum_{i=1}^k \Delta U_i = \sum_{i=1}^k m_i \Delta u_i = \sum_{i=1}^k N_i \Delta \bar{u}_i \quad (\text{kJ})$$

$$\Delta H_m = \sum_{i=1}^k \Delta H_i = \sum_{i=1}^k m_i \Delta h_i = \sum_{i=1}^k N_i \Delta \bar{h}_i \quad (\text{kJ})$$

$$\Delta S_m = \sum_{i=1}^k \Delta S_i = \sum_{i=1}^k m_i \Delta s_i = \sum_{i=1}^k N_i \Delta \bar{s}_i \quad (\text{kJ/K})$$

The internal energy, enthalpy, and entropy of a mixture per unit mass or per unit mole of the mixture can be determined by dividing the equations above by the mass or the mole number of the mixture (m_m or N_m).

$$u_m = \sum_{i=1}^k m f_i u_i \quad (\text{kJ/kg}) \quad \text{and} \quad \bar{u}_m = \sum_{i=1}^k y_i \bar{u}_i \quad (\text{kJ/kmol})$$

$$h_m = \sum_{i=1}^k m f_i h_i \quad (\text{kJ/kg}) \quad \text{and} \quad \bar{h}_m = \sum_{i=1}^k y_i \bar{h}_i \quad (\text{kJ/kmol})$$

$$s_m = \sum_{i=1}^k m f_i s_i \quad (\text{kJ/kg} \cdot \text{K}) \quad \text{and} \quad \bar{s}_m = \sum_{i=1}^k y_i \bar{s}_i \quad (\text{kJ/kmol} \cdot \text{K})$$

Similarly, the specific heats of a gas mixture can be expressed as

$$c_{v,m} = \sum_{i=1}^k m f_i c_{v,i} \quad (\text{kJ/kg} \cdot \text{K}) \quad \text{and} \quad \bar{c}_{v,m} = \sum_{i=1}^k y_i \bar{c}_{v,i} \quad (\text{kJ/kmol} \cdot \text{K})$$

$$c_{p,m} = \sum_{i=1}^k m f_i c_{p,i} \quad (\text{kJ/kg} \cdot \text{K}) \quad \text{and} \quad \bar{c}_{p,m} = \sum_{i=1}^k y_i \bar{c}_{p,i} \quad (\text{kJ/kmol} \cdot \text{K})$$

Ex.3/ An insulated rigid tank is divided into two compartments by a partition, as shown in Fig. below . One compartment contains 7 kg of oxygen gas at 40°C and 100 kPa, and the other compartment contains 4 kg of nitrogen gas at 20°C and 150 kPa. Now the partition is removed, and the two gases are allowed to mix. Determine (a) the mixture temperature and (b) the mixture pressure after equilibrium has been established.

(a) Noting that there is no energy transfer to or from the tank, the energy balance for the system can be expressed as

$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$$

$$0 = \Delta U = \Delta U_{\text{N}_2} + \Delta U_{\text{O}_2}$$

$$[mc_v(T_m - T_1)]_{\text{N}_2} + [mc_v(T_m - T_1)]_{\text{O}_2} = 0$$

By using c_v values at room temperature, the final temperature of the mixture is determined to be

$$(4 \text{ kg})(0.743 \text{ kJ/kg} \cdot \text{K})(T_m - 20^\circ\text{C}) + (7 \text{ kg})(0.658 \text{ kJ/kg} \cdot \text{K})(T_m - 40^\circ\text{C}) = 0$$

$$T_m = 32.2^\circ\text{C}$$

(b) The final pressure of the mixture is determined from the ideal-gas relation

$$P_m V_m = N_m R_u T_m$$

where

$$N_{\text{O}_2} = \frac{m_{\text{O}_2}}{M_{\text{O}_2}} = \frac{7 \text{ kg}}{32 \text{ kg/kmol}} = 0.219 \text{ kmol}$$

$$N_{\text{N}_2} = \frac{m_{\text{N}_2}}{M_{\text{N}_2}} = \frac{4 \text{ kg}}{28 \text{ kg/kmol}} = 0.143 \text{ kmol}$$

$$N_m = N_{\text{O}_2} + N_{\text{N}_2} = 0.219 + 0.143 = 0.362 \text{ kmol}$$

and

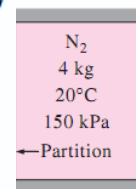
$$V_{\text{O}_2} = \left(\frac{NR_u T_1}{P_1} \right)_{\text{O}_2} = \frac{(0.219 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(313 \text{ K})}{100 \text{ kPa}} = 5.70 \text{ m}^3$$

$$V_{\text{N}_2} = \left(\frac{NR_u T_1}{P_1} \right)_{\text{N}_2} = \frac{(0.143 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(293 \text{ K})}{150 \text{ kPa}} = 2.32 \text{ m}^3$$

$$V_m = V_{\text{O}_2} + V_{\text{N}_2} = 5.70 + 2.32 = 8.02 \text{ m}^3$$

Thus,

$$P_m = \frac{N_m R_u T_m}{V_m} = \frac{(0.362 \text{ kmol})(8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K})(305.2 \text{ K})}{8.02 \text{ m}^3} = 114.5 \text{ kPa}$$

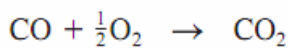
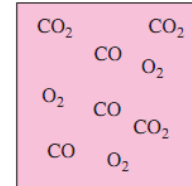


CHEMICAL AND PHASE EQUILIBRIUM

1- CRITERION FOR CHEMICAL EQUILIBRIUM

Consider a reaction chamber that contains a mixture of CO, O₂, and CO₂ at a specified temperature and pressure. Let us try to predict what will happen in this chamber (Fig.1). Probably the first thing that comes to mind is a chemical reaction between CO and O₂ to form more CO₂:

FIG.1
A reaction chamber that contains a mixture of CO₂, CO, and O₂ at a specified temperature and pressure.



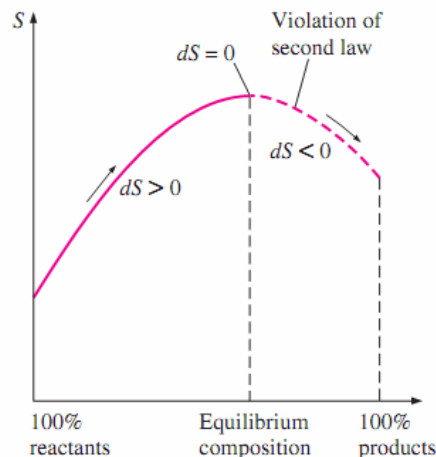
This reaction is certainly a possibility, but it is not the only possibility. It is also possible that some CO₂ in the combustion chamber dissociated into CO and O₂.

Taking the positive direction of heat transfer to be to the system, the increase of entropy principle for a reacting or non-reacting system

$$dS_{\text{sys}} \geq \frac{\delta Q}{T}$$

A system and its surroundings form an adiabatic system, and for such systems. Reduces to $dS_{\text{sys}} \geq 0$. That is, a chemical reaction in an adiabatic chamber proceeds in the direction of increasing entropy. When the entropy reaches a maximum, the reaction stops (Fig. 2). Therefore, entropy is a very useful property in the analysis of reacting adiabatic systems

FIGURE 2
Equilibrium criteria for a chemical reaction that takes place adiabatically

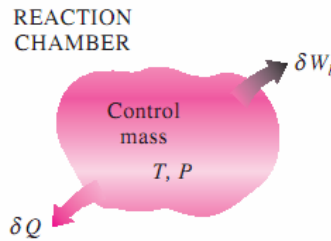


Consider a reacting (or non-reacting) simple compressible system of fixed mass with only quasi-equilibrium work modes at a specified temperature T and pressure P (Fig.3). Combining the first- and the second-law relations for this system give

$$\left. \begin{array}{l} \delta Q - P dV = dU \\ dS \geq \frac{\delta Q}{T} \end{array} \right\} dU + P dV - T ds \leq 0$$

FIGURE 3

A control mass undergoing a chemical reaction at a specified temperature and pressure.



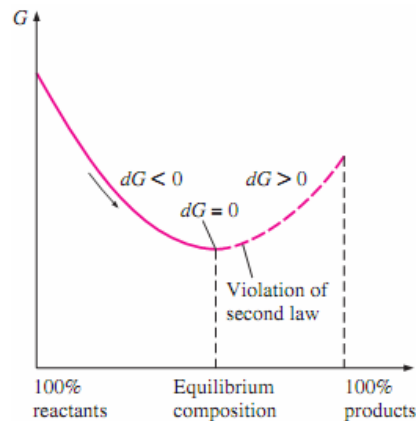
The differential of the Gibbs function ($G = H - TS$) at constant temperature and pressure is

$$\begin{aligned}(dG)_{T,P} &= dH - T dS - S dT \\ &= (dU + P dV + V dP) - T dS - S dT \\ &= dU + P dV - T dS\end{aligned}$$

we have $(dG)_{T,P} \leq 0$. Therefore, a chemical reaction at a specified temperature and pressure proceeds in the direction of a decreasing Gibbs function. The reaction stops and chemical equilibrium is established when the Gibbs function attains a minimum value (Fig. 4)

FIGURE 4

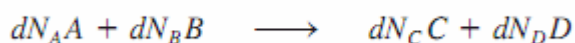
Criteria for chemical equilibrium for a fixed mass at a specified temperature and pressure



Therefore, the criterion for chemical equilibrium can be expressed as $(dG)_{T,P} = 0$

A chemical reaction at a specified temperature and pressure cannot proceed in the direction of the increasing Gibbs function since this will be a violation of the second law of thermodynamics.

Notice that if the temperature or the pressure is changed, the reacting system will assume a different equilibrium state, which is the state of the minimum Gibbs function at the new temperature or pressure. To obtain a relation for chemical equilibrium in terms of the properties of the individual components, consider a mixture of four chemical components A, B, C, and D that exist in equilibrium at a specified temperature and pressure. Let the number of moles of the respective components be N_A , N_B , N_C , and N_D . Now consider a reaction that occurs to an infinitesimal extent during which differential amounts of A and B (reactants) are converted to C and D (products) while the temperature and the pressure remain constant (Fig.5):



The equilibrium criterion requires that the change in the Gibbs function of the mixture during this process be equal to zero. That is

$$(dG)_{T,P} = \sum (dG_i)_{T,P} = \sum (\bar{g}_i dN_i)_{T,P} = 0$$

or

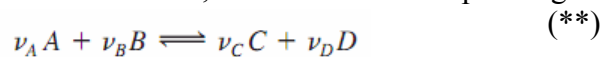
$$\bar{g}_C dN_C + \bar{g}_D dN_D + \bar{g}_A dN_A + \bar{g}_B dN_B = 0$$

FIGURE 5
An infinitesimal reaction in a chamber
at constant temperature and pressure

REACTION CHAMBER
T, P
N_A moles of A
N_B moles of B
N_C moles of C
N_D moles of D
$-dN_A A + dN_B B \rightarrow dN_C C + dN_D D$

where the \bar{g} are the molar Gibbs functions (also called the chemical potentials) at the specified temperature and pressure and the dN are the differential changes in the number of moles of the components.

To find a relation between the dN , we write the corresponding stoichiometric (theoretical) reaction



where the ν are the stoichiometric coefficients, which are evaluated easily once the reaction is specified. The stoichiometric reaction plays an important role in the determination of the equilibrium composition of the reacting mixtures because the changes in the number of moles of the components are proportional to the stoichiometric coefficients (Fig.6)

FIGURE 6
The changes in the number of moles
of the components during a chemical
reaction are proportional to the
stoichiometric coefficients regardless
of the extent of the reaction.

$H_2 \rightarrow 2H$
$0.1H_2 \rightarrow 0.2H$
$0.01H_2 \rightarrow 0.02H$
$0.001H_2 \rightarrow 0.002H$
$\nu_{H_2} = 1$
$\nu_H = 2$

$$\begin{aligned} dN_A &= -\epsilon \nu_A & dN_C &= \epsilon \nu_C \\ dN_B &= -\epsilon \nu_B & dN_D &= \epsilon \nu_D \end{aligned}$$

where ϵ the proportionality constant and represents the extent of a reaction. A minus sign is added to the first two terms because the number of moles of the reactants A and B decreases as the reaction progresses.

2 -THE EQUILIBRIUM CONSTANT FOR IDEAL-GAS MIXTURES

Consider a mixture of ideal gases that exists in equilibrium at a specified temperature and pressure. Like entropy, the Gibbs function of an ideal gas depends on both the temperature and the pressure. The variation of the Gibbs function of an ideal gas with pressure at a fixed temperature is determined by using the definition of the Gibbs function ($\bar{g} = \bar{h} - T\bar{s}$) and the entropy-change relation for isothermal processes [$\Delta \bar{s} = -R_u \ln(P_2/P_1)$]. It yields

$$(\Delta \bar{g})_T = \Delta \bar{h} \xrightarrow{0} T(\Delta \bar{s})_T = -T(\Delta \bar{s})_T = R_u T \ln \frac{P_2}{P_1}$$

Thus the Gibbs function of component i of an ideal-gas mixture at its partial pressure P_i and mixture temperature T can $\bar{g}_i(T, P_i) = \bar{g}_i^*(T) + R_u T \ln P_i$

where $\bar{g}_i^*(T)$ represents the Gibbs function of component i at 1 atm pressure and temperature T , and P_i

represents the partial pressure of component i in atmospheres. Substituting the Gibbs function expression into Eq. (**), we obtain

$$\begin{aligned} \nu_C [\bar{g}_C^*(T) + R_u T \ln P_C] + \nu_D [\bar{g}_D^*(T) + R_u T \ln P_D] \\ - \nu_A [\bar{g}_A^*(T) + R_u T \ln P_A] - \nu_B [\bar{g}_B^*(T) + R_u T \ln P_B] = 0 \end{aligned}$$

For convenience, we define the **standard-state Gibbs function change** as

$$\Delta G^*(T) = \nu_C \bar{g}_C^*(T) + \nu_D \bar{g}_D^*(T) - \nu_A \bar{g}_A^*(T) - \nu_B \bar{g}_B^*(T)$$

Substituting, we get

$$\Delta G^*(T) = -R_u T (\nu_C \ln P_C + \nu_D \ln P_D - \nu_A \ln P_A - \nu_B \ln P_B) = -R_u T \ln \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} \quad (*)$$

Now we define the **equilibrium constant K_P** for the chemical equilibrium of ideal-gas mixtures as

$$K_P = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}}$$

Substituting into Eq. (*) and rearranging, we obtain

$$K_P = e^{-\Delta G^*(T)/R_u T} \quad (1)$$

Once the equilibrium constant is available, it can be used to determine the equilibrium composition of reacting ideal-gas mixtures. This is accomplished by expressing the partial pressures of the components in terms of their mole fractions

$$P_i = y_i P = \frac{N_i}{N_{\text{total}}} P$$

where P is the total pressure and N_{total} is the total number of moles present in the reaction chamber, including any *inert gases*. Replacing the partial pressures the above relation and rearranging, we obtain (Fig. 7)

$$K_P = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{total}} \right)^{\Delta \nu}$$

where

$$\Delta \nu = \nu_C + \nu_D - \nu_A - \nu_B$$

FIGURE 7
Three equivalent K_P relations for
reacting ideal-gas mixtures

(1) In terms of partial pressures

$$K_P = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}}$$

(2) In terms of $\Delta G^*(T)$

$$K_P = e^{-\Delta G^*(T)/R_u T}$$

(3) In terms of the equilibrium composition

$$K_P = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{total}} \right)^{\Delta \nu}$$

Ex/1, Using Eq. 1 and the Gibbs function data, determine the equilibrium constant K_P for the dissociation process $N_2 \rightarrow 2N$ at 25°C. Compare your result to the K_P value listed in Table?

Properties The equilibrium constant of this reaction at 298 K is $\ln K_P = -367.5$ (Table A-28). The Gibbs function of formation at 25°C and 1 atm is 0 for N_2 and 455,510 kJ/kmol for N (Table A-26).

$$K_P = e^{-\Delta G^*(T)/R_u T}$$

where, from Eq. 16-11,

$$\begin{aligned} \Delta G^*(T) &= \nu_N \bar{g}_N^*(T) - \nu_{N_2} \bar{g}_{N_2}^*(T) \\ &= (2)(455,510 \text{ kJ/kmol}) - 0 \\ &= 911,020 \text{ kJ/kmol} \end{aligned}$$

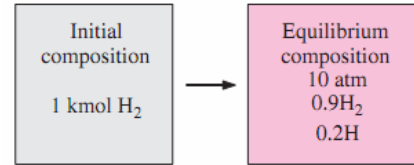
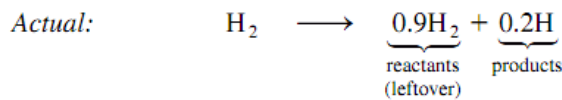
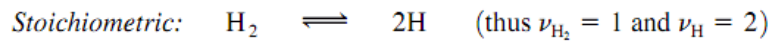
Substituting, we find

$$\begin{aligned} \ln K_P &= -\frac{911,020 \text{ kJ/kmol}}{(8.314 \text{ kJ/kmol} \cdot \text{K})(298.15 \text{ K})} \\ &= -367.5 \end{aligned}$$

or

$$K_P \cong 2 \times 10^{-160}$$

Ex2:- Determine the temperature at which 10 percent of diatomic hydrogen (H₂) dissociates into monatomic hydrogen (H) at a pressure of 10 atm.



A double-headed arrow is used for the stoichiometric reaction to differentiate it from the actual reaction. This reaction involves one reactant (H₂) and one product (H). The equilibrium composition consists of 0.9 kmol of H₂ (the leftover reactant) and 0.2 kmol of H (the newly formed product).

Therefore, $N_{\text{H}_2} = 0.9$ and $N_{\text{H}} = 0.2$ and the equilibrium constant K_P is determined from

$$K_P = \frac{N_{\text{H}}^{\nu_{\text{H}}}}{N_{\text{H}_2}^{\nu_{\text{H}_2}}} \left(\frac{P}{N_{\text{total}}} \right)^{\nu_{\text{H}} - \nu_{\text{H}_2}} = \frac{(0.2)^2}{0.9} \left(\frac{10}{0.9 + 0.2} \right)^{2-1} = 0.404$$

From Table A-28, the temperature corresponding to this K_P value is

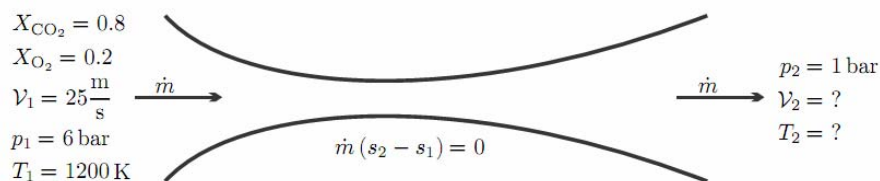
$$T = 3535 \text{ K}$$

H.W

We consider the isentropic expansion of a mixture of oxygen ($X_{\text{O}_2} = 0.2$) and carbon dioxide ($X_{\text{CO}_2} = 1 - X_{\text{O}_2} = 0.8$) entering a nozzle at $V_1 = 25 \text{ m/s}$, $p_1 = 6 \text{ bar}$, $T_1 = 1200 \text{ K}$ and leaving at $p_2 = 1 \text{ bar}$. Find the temperature T_2 and the velocity V_2 at the nozzle exit.

Given

The molar mass of the mixture is $M = X_{\text{O}_2}M_{\text{O}_2} + X_{\text{CO}_2}M_{\text{CO}_2} = 41.6 \text{ kg/kmol}$. Since the process is reversible and adiabatic, it is isentropic.



PHASE EQUILIBRIUM

Gibbs function, and the equilibrium criterion for a reacting or non-reacting system was expressed $(dG)_{T,P} = 0$

We know from experience that a wet T- shirt hanging in an open area eventually dries, a small amount of water left in a glass evaporates, and the aftershave in an open bottle quickly disappears (Fig. 1). These examples suggest that there is a driving force between the two phases of a substance that forces the mass to transform from one phase to another. The magnitude of this force depends, among other things, on the relative concentrations of the two phases. A wet T-shirt dries much quicker in dry air than it does in humid air. In fact, it does not dry at all if the relative humidity of the environment is 100 percent. In this case, there is no transformation from the liquid phase to the vapor phase, and the two phases are in phase equilibrium. The conditions of phase equilibrium change, however, if the temperature or the pressure is changed. Therefore, we examine phase equilibrium at a specified temperature and pressure.

FIGURE 1
Wet clothes hung in an open area eventually dry as a result of mass transfer from the liquid phase to the vapor phase.



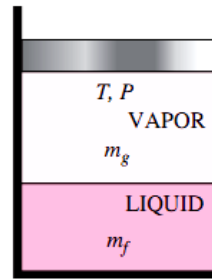
1- Phase Equilibrium for a Single-Component System

The equilibrium criterion for two phases of a pure substance such as water is easily developed by considering a mixture of saturated liquid and saturated vapor in equilibrium at a specified temperature and pressure, such as that shown in Fig. 2. The total Gibbs function of this mixture is

$$G = m_f g_f + m_g g_g$$

where g_f and g_g are the Gibbs functions of the liquid and vapor phases per unit mass, respectively. Now imagine a disturbance during which a differential amount of liquid dm_f evaporates at constant temperature and pressure.

FIGURE 2
A liquid–vapor mixture in equilibrium
at a constant temperature and pressure



The change in the total Gibbs function during this disturbance is

$$(dG)_{T,P} = g_f dm_f + g_g dm_g$$

since g_f and g_g remain constant at constant temperature and pressure. At equilibrium, $(dG)_{T,P} = 0$. Also from the conservation of mass, $dm_g = -dm_f$. Substituting, we obtain

$$(dG)_{T,P} = (g_f - g_g) dm_f$$

which must be equal to zero at equilibrium. It yields $g_f = g_g$

Therefore, the two phases of a pure substance are in equilibrium when each phase has the same value of specific Gibbs function. Also, at the triple point (the state at which all three phases coexist in equilibrium), the specific Gibbs functions of all three phases are equal to each other.

What happens if $g_f > g_g$? Obviously, the two phases are not in equilibrium at that moment. The second law requires that $(dG)_{T,P} = (g_f - g_g) dm_f \leq 0$. Thus, dm_f must be negative, which means that some liquid must vaporize until $g_f = g_g$. Therefore, the Gibbs function difference is the driving force for phase change, just as the temperature difference is the driving force for heat transfer.

EX.1/ Show that a mixture of saturated liquid water and saturated water vapor at 120°C satisfies the criterion for phase equilibrium.

ANS.

Properties The properties of saturated water at 120°C are $h_f = 503.81$ kJ/kg, $s_f = 1.5279$ kJ/kg · K, $h_g = 2706.0$ kJ/kg, and $s_g = 7.1292$ kJ/kg · K (Table A-4).

Analysis Using the definition of Gibbs function together with the enthalpy and entropy data, we have

$$\begin{aligned} g_f &= h_f - Ts_f = 503.81 \text{ kJ/kg} - (393.15 \text{ K})(1.5279 \text{ kJ/kg} \cdot \text{K}) \\ &= -96.9 \text{ kJ/kg} \end{aligned}$$

and

$$\begin{aligned} g_g &= h_g - Ts_g = 2706.0 \text{ kJ/kg} - (393.15 \text{ K})(7.1292 \text{ kJ/kg} \cdot \text{K}) \\ &= -96.8 \text{ kJ/kg} \end{aligned}$$

2- The Phase Rule

Notice that a single-component two-phase system may exist in equilibrium at different temperatures (or pressures). However, once the temperature is fixed, the system is locked into an equilibrium state and all intensive properties of each phase (except their relative amounts) are fixed. Therefore, a single-component two-phase system has one independent property, which may be taken to be the temperature or the pressure.

In general, the number of independent variables associated with a multicomponent, multiphase system is given by the Gibbs phase rule, expressed as:-

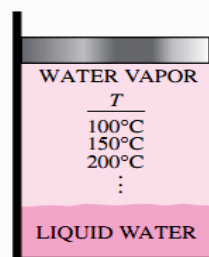
$$IV = C - PH + 2$$

where IV = the number of independent variables, C = the number of components, and PH = the number of phases present in equilibrium.

For the single-component (C = 1) two-phase (PH = 2) system discussed above, for example, one independent intensive property needs to be specified (IV = 1, Fig. 3).

FIGURE 3

According to the Gibbs phase rule, a single-component, two-phase system can have only one independent variable



3- Phase Equilibrium for a Multicomponent System

Many multiphase systems encountered in practice involve two or more components. A multicomponent multiphase system at a specified temperature and pressure is in phase equilibrium when there is no driving force between the different phases of each component. Thus, for phase equilibrium, the specific Gibbs function of each component must be the same in all phases (Fig. 4). That is,

$$g_{f,1} = g_{g,1} = g_{s,1} \quad \text{for component 1}$$

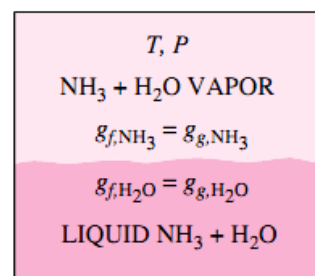
$$g_{f,2} = g_{g,2} = g_{s,2} \quad \text{for component 2}$$

.....

$$g_{f,N} = g_{g,N} = g_{s,N} \quad \text{for component } N$$

FIGURE 4

A multicomponent multiphase system is in phase equilibrium when the specific Gibbs function of each component is the same in all phases.



Some components may exist in more than one solid phase at the specified temperature and pressure. In this case, the specific Gibbs function of each solid phase of a component must also be the same for phase equilibrium. The phase equilibrium of two-component systems that involve two phases (liquid and vapor) in equilibrium. For such systems, $C = 2$, $PH = 2$, and thus $IV = 2$. That is, a two-component, two-phase system has two independent variables, and such a system will not be in equilibrium unless two independent intensive properties are fixed.

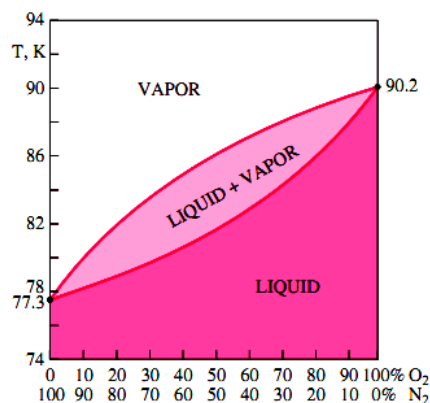
That is, the mole fraction of a component is different in different phases. This is illustrated in Fig.5, for the two-phase mixture of oxygen and nitrogen at a pressure of 0.1 MPa. On this diagram, the vapor line represents the equilibrium composition of the vapor phase at various temperatures, and the liquid line does the same for the liquid phase. At 84 K, for example, the mole fractions are 30 percent nitrogen and 70 percent oxygen in the liquid phase and 66 percent nitrogen and 34 percent oxygen in the vapor phase. Notice that

$$y_{f,N_2} + y_{f,O_2} = 0.30 + 0.70 = 1$$

$$y_{g,N_2} + y_{g,O_2} = 0.66 + 0.34 = 1$$

FIGURE 5

Equilibrium diagram for the two-phase mixture of oxygen and nitrogen at 0.1 MPa

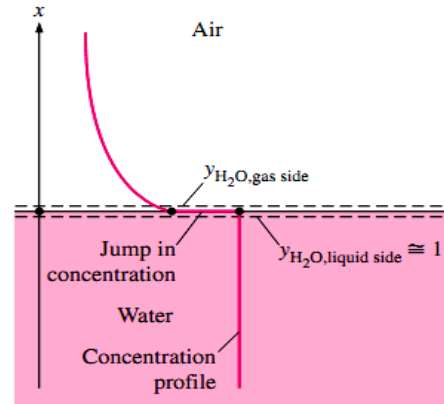


The water and air temperatures at the free surface of a lake, for example, are always the same. The mole fractions of air on the two sides of a water–air interface, however, are obviously very different (in fact, the mole fraction of air in water is close to zero). Likewise, the mole fractions of water on the two sides of a water–air interface are also different even when air is saturated (Fig. 6). Therefore, when specifying mole fractions in two-phase mixtures, we need to clearly specify the intended phase.

In most practical applications, the two phases of a mixture are not in phase equilibrium since the establishment of phase equilibrium requires the diffusion of species from higher concentration regions to lower concentration regions, which may take a long time.

FIGURE 6

Unlike temperature, the mole fraction of species on the two sides of a liquid–gas (or solid–gas or solid–liquid) interface are usually not the same.



A certain amount of solid can be dissolved in a liquid, and the solubility of the solid in the liquid is determined from the requirement that thermodynamic equilibrium exists between the solid and the solution at the interface.

The solubility represents the maximum amount of solid that can be dissolved in a liquid at a specified temperature. In Table 1 we present sample solubility data for sodium chloride (NaCl) and calcium bicarbonate [Ca(HCO₃)₂] at various temperatures. For example, the solubility of salt (NaCl) in water at 310 K is 36.5 kg per 100 kg of water. Therefore, the mass fraction of salt in the saturated brine is simply.

$$mf_{\text{salt,liquid side}} = \frac{m_{\text{salt}}}{m} = \frac{36.5 \text{ kg}}{(100 + 36.5) \text{ kg}} = 0.267 \text{ (or 26.7 percent)}$$

dilute solutions the mole fractions of a species *i* in the gas and liquid phases at the interface are observed to be proportional to each other

This is known as the **Henry's law** and is expressed as

$$y_{i,\text{liquid side}} = \frac{P_{i,\text{gas side}}}{H}$$

where *H* is the **Henry's constant**, which is the product of the total pressure of the gas mixture and the proportionality constant.

TABLE 1
Solubility of two inorganic compounds in water at various temperatures, in kg (in 100 kg of water

Temperature, K	Solute	
	Salt NaCl	Calcium bicarbonate Ca(HCO ₃) ₂
273.15	35.7	16.15
280	35.8	16.30
290	35.9	16.53
300	36.2	16.75
310	36.5	16.98
320	36.9	17.20
330	37.2	17.43
340	37.6	17.65
350	38.2	17.88
360	38.8	18.10
370	39.5	18.33
373.15	39.8	18.40

Values of the Henry's constant for a number of aqueous solutions are given in Table 2 for various temperatures.

TABLE 2

Henry's constant H (in bars) for selected gases in water at low to moderate pressures (for gas i , $H = P_{i,\text{gas side}}/y_{i,\text{water side}}$) (from Mills, Table A.21, p. 874)

Solute	290 K	300 K	310 K	320 K	330 K	340 K
H ₂ S	440	560	700	830	980	1140
CO ₂	1,280	1,710	2,170	2,720	3,220	—
O ₂	38,000	45,000	52,000	57,000	61,000	65,000
H ₂	67,000	72,000	75,000	76,000	77,000	76,000
CO	51,000	60,000	67,000	74,000	80,000	84,000
Air	62,000	74,000	84,000	92,000	99,000	104,000
N ₂	76,000	89,000	101,000	110,000	118,000	124,000

Henry's law is limited to dilute gas–liquid solutions, that is, liquids with a small amount of gas dissolved in them. Then the question that arises naturally is, what do we do when the gas is highly soluble in the liquid (or solid), such as ammonia in water? In this case, the linear relationship of *Henry's law* does not apply, and the mole fraction of a gas dissolved in the liquid (or solid) is usually expressed as a function of the partial pressure of the gas in the gas phase and the temperature. An approximate relation in this case for the mole fractions of a species on the liquid and gas sides of the interface is given by ***Raoult's law*** as

$$P_{i,\text{gas side}} = y_{i,\text{gas side}} P_{\text{total}} = y_{i,\text{liquid side}} P_{i,\text{sat}}(T)$$

where $P_{i,\text{sat}}(T)$ is the saturation pressure of the species i at the interface temperature and P_{total} is the total pressure on the gas phase side.

The molar density of the gas species i in the solid at the interface $\bar{\rho}_{i,\text{solid side}}$ is proportional to the partial pressure of the species i in the gas $P_{i,\text{gas side}}$ on the gas side of the interface and is expressed as

$$\bar{\rho}_{i,\text{solid side}} = \mathcal{S} \times P_{i,\text{gas side}} \quad (\text{kmol/m}^3)$$

Where \mathcal{S} is the solubility

Expressing the pressure in bars and noting that the unit of molar concentration is kmol of species i per m³, the unit of solubility is kmol/m³ · bar. Solubility data for selected gas–solid combinations are given in Table 3

TABLE 3
Solubility of selected gases and
solids (from Barrer)

(for gas i , $\mathcal{S} = \bar{\rho}_{i,\text{solid side}}/P_{i,\text{gas side}}$)

\mathcal{S}			
Gas	Solid	T K	kmol/m ³ · bar
O ₂	Rubber	298	0.00312
N ₂	Rubber	298	0.00156
CO ₂	Rubber	298	0.04015
He	SiO ₂	298	0.00045
H ₂	Ni	358	0.00901

Ex1:- Determine the mole fraction of the water vapor at the surface of a lake whose temperature is 15°C, and compare it to the mole fraction of water in the lake (Fig below). Take the atmospheric pressure at lake level to be 92 kPa.

ANS

The air at the water surface is saturated. Therefore, the partial pressure of water vapor in the air at the lake surface will simply be the saturation pressure of water at 15°C,

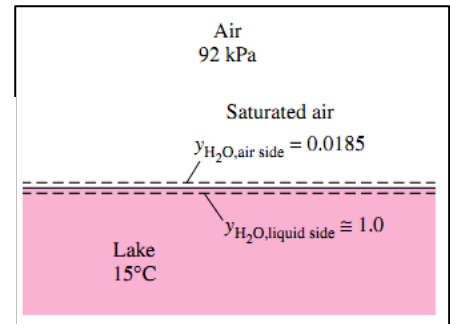
$$P_v = P_{\text{sat @ 15°C}} = 1.7057 \text{ kPa}$$

The mole fraction of water vapor in the air at the surface of the lake is determined

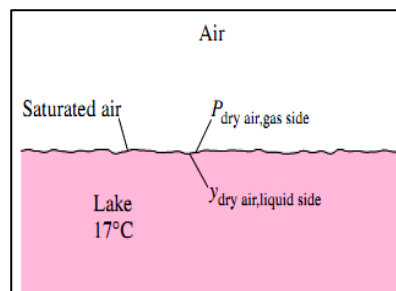
$$y_v = \frac{P_v}{P} = \frac{1.7057 \text{ kPa}}{92 \text{ kPa}} = \mathbf{0.0185 \text{ or } 1.85 \text{ percent}}$$

Water contains some dissolved air, but the amount is negligible. Therefore, we can assume the entire lake to be liquid water. Then its mole fraction becomes

$$y_{\text{water,liquid side}} \cong \mathbf{1.0 \text{ or } 100 \text{ percent}}$$



EX2:- Determine the mole fraction of air at the surface of a lake whose temperature is 17°C (Fig. below). Take the atmospheric pressure at lake level to be 92 kPa



ANS

$$P_v = P_{\text{sat}} @ 17^\circ\text{C} = 1.96 \text{ kPa}$$

The partial pressure of dry air is

$$P_{\text{dry air}} = P - P_v = 92 - 1.96 = 90.04 \text{ kPa} = 0.9004 \text{ bar}$$

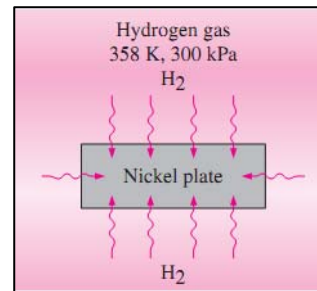
Note that we could have ignored the vapor pressure since the amount of vapor in air is so small with little loss in accuracy (an error of about 2 percent). The mole fraction of air in the water is, from Henry's law,

$$y_{\text{dry air, liquid side}} = \frac{P_{\text{dry air, gas side}}}{H} = \frac{0.9004 \text{ bar}}{62,000 \text{ bar}} = 1.45 \times 10^{-5}$$

EX3:- Consider a nickel plate that is placed into a tank filled with hydrogen gas at 358 K and 300 kPa. Determine the molar and mass density of hydrogen in the nickel plate when phase equilibrium is established (Fig. below).

ANS

The molar mass of hydrogen H_2 is $M = 2 \text{ kg/kmol}$, and the solubility of hydrogen in nickel at the specified temperature is given in Table 3 to be $0.00901 \text{ kmol/m}^3 \cdot \text{bar}$.



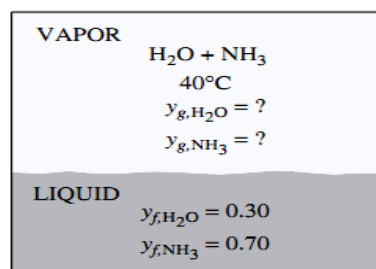
$$\begin{aligned} \bar{\rho}_{\text{H}_2, \text{solid side}} &= \mathcal{S} \times P_{\text{H}_2, \text{gas side}} \\ &= (0.00901 \text{ kmol/m}^3 \cdot \text{bar})(3 \text{ bar}) = 0.027 \text{ kmol/m}^3 \end{aligned}$$

It corresponds to a mass density of

$$\begin{aligned} \rho_{\text{H}_2, \text{solid side}} &= \bar{\rho}_{\text{H}_2, \text{solid side}} M_{\text{H}_2} \\ &= (0.027 \text{ kmol/m}^3)(2 \text{ kg/kmol}) = 0.054 \text{ kg/m}^3 \end{aligned}$$

That is, there will be 0.027 kmol (or 0.054 kg) of H_2 gas in each m^3 volume of nickel plate when phase equilibrium is established.

EX4:- In absorption refrigeration systems, a two-phase equilibrium mixture of liquid ammonia (NH_3) and water (H_2O) is frequently used. Consider one such mixture at 40°C , shown in Fig. below. If the composition of the liquid phase is 70 percent NH_3 and 30 percent H_2O by mole numbers, determine the composition of the vapor phase of this mixture.



ANS

Properties The saturation pressures of H₂O and NH₃ at 40°C are $P_{\text{H}_2\text{O},\text{sat}} = 7.3851 \text{ kPa}$ and $P_{\text{NH}_3,\text{sat}} = 1554.33 \text{ kPa}$.

$$P_{\text{H}_2\text{O},\text{gas side}} = y_{\text{H}_2\text{O},\text{liquid side}} P_{\text{H}_2\text{O},\text{sat}}(T) = 0.30(7.3851 \text{ kPa}) = 2.22 \text{ kPa}$$

$$P_{\text{NH}_3,\text{gas side}} = y_{\text{NH}_3,\text{liquid side}} P_{\text{NH}_3,\text{sat}}(T) = 0.70(1554.33 \text{ kPa}) = 1088.03 \text{ kPa}$$

The total pressure of the mixture is

$$P_{\text{total}} = P_{\text{H}_2\text{O}} + P_{\text{NH}_3} = 2.22 + 1088.03 = 1090.25 \text{ kPa}$$

Then the mole fractions in the gas phase are

$$y_{\text{H}_2\text{O},\text{gas side}} = \frac{P_{\text{H}_2\text{O},\text{gas side}}}{P_{\text{total}}} = \frac{2.22 \text{ kPa}}{1090.25 \text{ kPa}} = 0.0020$$

$$y_{\text{NH}_3,\text{gas side}} = \frac{P_{\text{NH}_3,\text{gas side}}}{P_{\text{total}}} = \frac{1088.03 \text{ kPa}}{1090.25 \text{ kPa}} = 0.9980$$

INTRODUCTION TO POWER SYSTEMS

In introducing the second law of thermodynamics its considered cyclic heat engines consisting of four separate processes, that these engines can be operated as steady-state devices involving shaft work, or as cylinder/piston devices involving boundary-movement work. The former may have a working fluid that changes phase during the processes in the cycle or may have a single-phase working fluid throughout.

For a reversible steady-state process involving negligible kinetic and potential energy changes, the shaft work per unit mass is given by

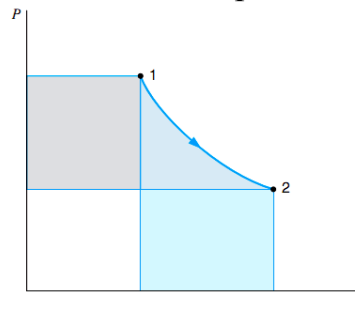
$$w = - \int v dP$$

For a reversible process involving a simple compressible substance, the boundary movement work per unit mass is given by

$$w = \int P dv$$

The areas represented by these two integrals are shown in Fig.1. It is of interest to note that, in the former case, there is no work involved in a constant-pressure process, while in the latter case, there is no work involved in a constant-volume process

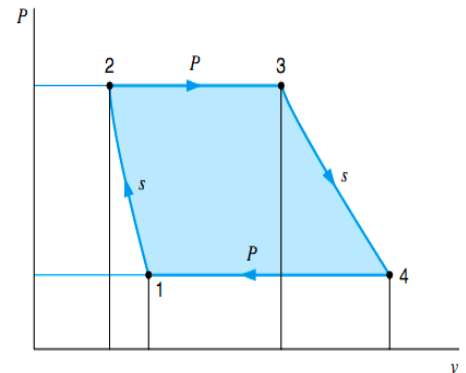
FIGURE 1
Comparison of shaft
work and boundary-
movement work



For convenience of operation, we will make the two heat-transfer processes (boiler and condenser) constant-pressure processes, such that those are simple heat exchangers involving no work. Let us also assume that the turbine and pump processes are both adiabatic and are therefore isentropic processes. Thus, the four processes comprising the cycle are as shown in Fig.2. Note that if the entire cycle takes place inside the two-phase liquid–vapor dome, the resulting cycle is the Carnot cycle, since the two constant-pressure processes are also isothermal. Otherwise, this cycle is not a Carnot cycle. In either case, it can be found that the net work output for this power system is given by

$$w_{\text{net}} = - \int_1^2 v dP + 0 - \int_3^4 v dP + 0 = - \int_1^2 v dP + \int_4^3 v dP$$

FIGURE 2
Four-process power cycle.



In the next several sections, we consider the Rankine cycle, which is the ideal four-steady-state process cycle shown in Fig.2, utilizing a phase change between vapor and liquid to maximize the difference in specific volume during expansion and compression. This is the idealized model for a steam power plant system.

2 THE RANKINE CYCLE

Now consider the idealized four-steady-state-process cycle shown in Fig.2, in which state 1 is saturated liquid and state 3 is either saturated vapor or superheated vapor. This system is termed the **Rankine cycle** and is the model for the simple steam power plant. It is convenient to show the states and processes on a T - s diagram, as given in Fig.3. The four processes are:

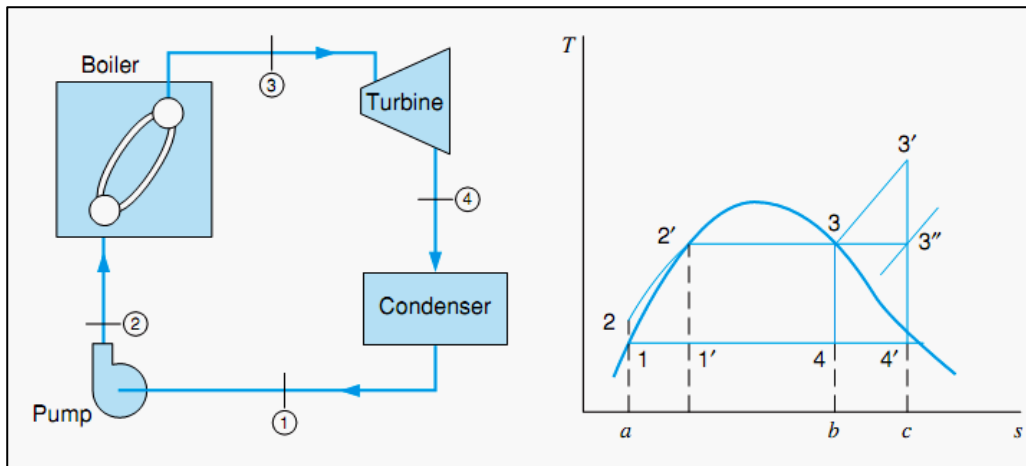


FIG. 3 Simple steam power plant that operates on the Rankine cycle.

1–2: Reversible adiabatic pumping process in the pump

2–3: Constant-pressure transfer of heat in the boiler

3–4: Reversible adiabatic expansion in the turbine (or another prime mover such as a steam engine)

4–1: Constant-pressure transfer of heat in the condenser

As mentioned earlier, the Rankine cycle also includes the possibility of superheating the vapor, as cycle 1–2–3'–4'–1.

If changes of kinetic and potential energy are neglected, heat transfer and work may be represented by various areas on the T - s diagram. The heat transferred to the working fluid is represented by area a –2–2'–3– b – a and the heat transferred from the working fluid by area a –1–4– b – a . From the energy equation we conclude that the area representing the work is the difference between these two areas—area 1–2–2'–3–4–1. The thermal efficiency is defined by the relation

$$\eta_{th} = \frac{w_{net}}{q_H} = \frac{\text{area } 1-2-2'-3-4-1}{\text{area } a-2-2'-3-b-a}$$

For analyzing the Rankine cycle, it is helpful to think of efficiency as depending on the average temperature at which heat is supplied and the average temperature at which heat is rejected. Any changes that increase the average temperature at which heat is supplied or decrease the average temperature at which heat is rejected will increase the Rankine-cycle efficiency.

Each process can be analyzed using the steady flow energy equation, ΔKE and ΔPE may be neglected.

i. e. $h_i + Q = h_e + W$

Boiler: $h_1 + Q_{4.5.1} = h_1 + W$

$W = 0$, $Q_{4.5.1} = h_1 - h_4$

Turbine: $h_1 + {}_1Q_2 = h_2 + {}_1W_2$

$Q = 0$, ${}_1W_2 = h_1 - h_2$

Condenser: $h_2 + {}_2Q_3 = h_3 + W$

since $W = 0$, ${}_2Q_3 = -(h_2 - h_3)$

\therefore heat rejected in condenser $= h_2 - h_3$

Pump: $h_3 + {}_3Q_4 = h_4 + {}_3W_4$

$Q = 0$, ${}_3W_4 = h_3 - h_4 = -(h_4 - h_3)$

Work input to pump $= (h_4 - h_3)$

${}_3W_4$ is a small quantity in comparison with ${}_1W_2$. Hence, it is usually neglected (especially when boiler pr. are low).

Net work don in the cycle, $W_{net} = {}_1W_2 - {}_3W_4$

$$W = (h_1 - h_2) - (h_4 - h_3)$$

Or, if the feed pump work (${}_3W_4$) is neglected,

$$W = (h_1 - h_2)$$

The heat supplied in the boiler, $Q_{4.5.1} = h_1 - h_4$

Rankine efficincy $\zeta_R = \frac{\text{net work output}}{\text{heat supplied in the boiler}}$

$$\begin{aligned}\zeta_R &= \frac{(h_1 - h_2) - (h_4 - h_3)}{(h_1 - h_4)} \\ &= \frac{(h_1 - h_2) - (h_4 - h_3)}{(h_1 - h_3) - (h_4 - h_3)}\end{aligned}$$

if the feed pump work ($h_4 - h_3$) is neglected:

$$\zeta_R = \frac{(h_1 - h_2)}{(h_1 - h_3)}$$

* When the feed pump work is to be included it is necessary to determine the quantity (${}_3W_4$)

$$\text{Pump work} = -{}_3W_4 = (h_4 - h_3)$$

** For liquid which is assumed to be incompressible (i.e. $V=\text{Constant}$):

$$h_4 - h_3 = v (P_4 - P_3)$$

Where (v) can be taken from tables for water at pressure P_3 .

Ex1:- Determine the efficiency of a Rankine cycle using steam as the working fluid in which the condenser pressure is 10 kPa. The boiler pressure is 2 MPa. The steam leaves the boiler as saturated vapor.

Ans.

Assuming the liquid to be incompressible, we have

$$w_p = v(P_2 - P_1) = 0.00101 \text{ m}^3/\text{kg} (2000 - 10) \text{ kPa} = 2.0 \text{ kJ/kg}$$

$$h_2 = h_1 + w_p = 191.8 + 2.0 = 193.8 \text{ kJ/kg}$$

Substituting, we obtain

$$q_H = h_3 - h_2 = 2799.5 - 193.8 = 2605.7 \text{ kJ/kg}$$

Turning to the turbine next, we have:

Control volume: Turbine.

Inlet state: State 3 known (above).

Exit state: P_4 known.

We can determine the quality at state 4 as follows:

$$s_3 = s_4 = 6.3409 = 0.6493 + x_4 7.5009, \quad x_4 = 0.7588$$

$$h_4 = 191.8 + 0.7588(2392.8) = 2007.5 \text{ kJ/kg}$$

$$w_t = 2799.5 - 2007.5 = 792.0 \text{ kJ/kg}$$

Finally, we consider the condenser.

Control volume: Condenser.

Inlet state: State 4 known (as given).

Exit state: State 1 known (as given).

Substituting, we obtain

$$q_L = h_4 - h_1 = 2007.5 - 191.8 = 1815.7 \text{ kJ/kg}$$

We can now calculate the thermal efficiency:

$$\eta_{th} = \frac{w_{net}}{q_H} = \frac{q_H - q_L}{q_H} = \frac{w_t - w_p}{q_H} = \frac{792.0 - 2.0}{2605.7} = 30.3\%$$

We could also write an expression for thermal efficiency in terms of properties at various points in the cycle:

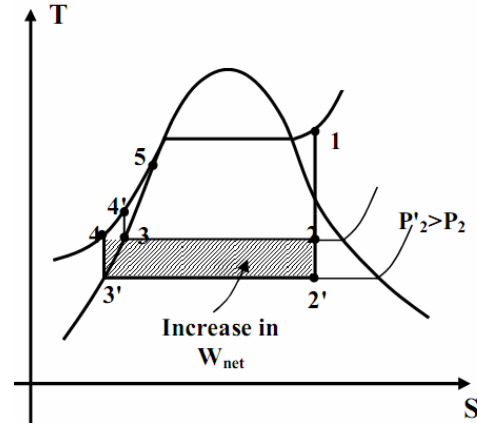
$$\begin{aligned} \eta_{th} &= \frac{(h_3 - h_2) - (h_4 - h_1)}{h_3 - h_2} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2} \\ &= \frac{2605.7 - 1815.7}{2605.7} = \frac{792.0 - 2.0}{2605.7} = 30.3\% \end{aligned}$$

How can we increase the efficiency of the Rankine cycle

Steam power plants are used for the production of most of the electric power in the world, therefore, as small increases in thermal efficiency can mean large savings from the fuel requirement.

1- Lowering the condenser pressure:

The dashed area in this diagram represents the increase in W_{net} . The heat input also increases (represented by the area under curve 4 - 4'), but this increase is very small. Thus, the overall effect of lowering the condenser pressure is an increase in the thermal efficiency of the cycle.



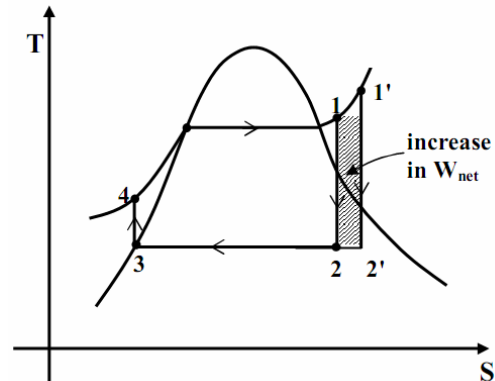
Disadvantages:

- 1- It creates the problem of air leakage into the condenser.
- 2- It increases the moisture content of the steam at the final-stages of the turbine. The large quantities of moisture are highly undesirable because it erodes the turbine blades.

2- Superheating the steam to high temperature:

Both the W_{net} and heat input increase as a result of superheating. The overall effect is an increase in (ζR) .

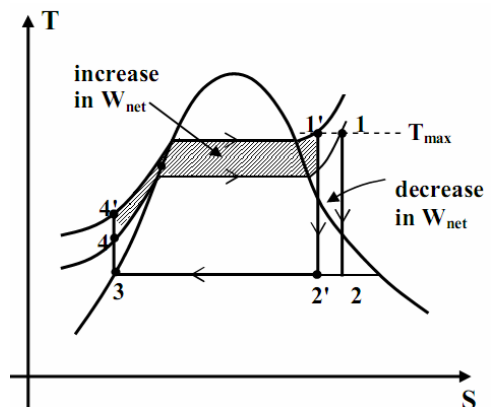
* Superheating decreasing the moisture content of the steam at the turbine exit as shown in T-S diagram (the quality (x) at state 2' is higher than that at state 2).



** Presently the highest steam temperature allowed at the turbine inlet is about 620 c°. Any increase in this value depends on improving the present material of the blades.

3- Increasing the boiler pressure:

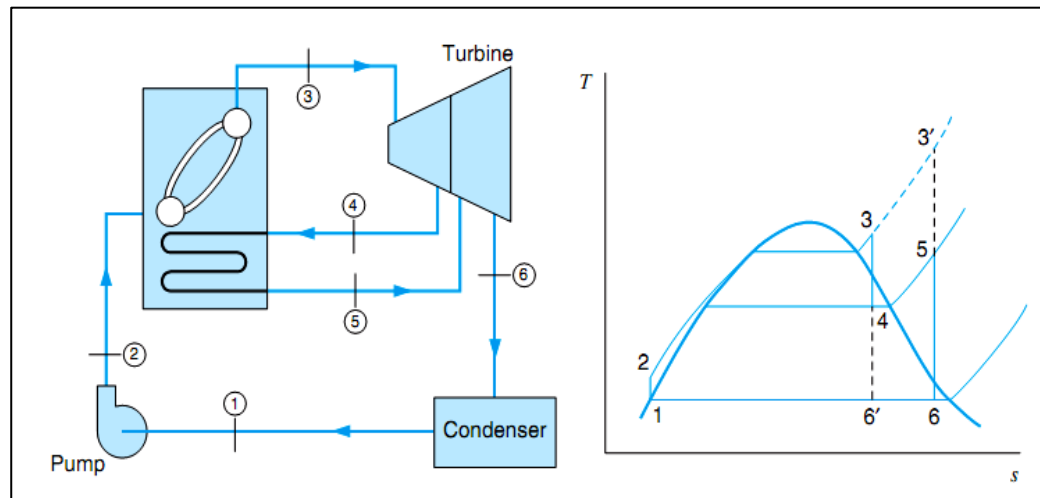
It raises the average temp. at which heat is added to the steam and thus, raises the (ζ) . For a fixed turbine inlet temp., the cycle shifts to the left and the moisture content of the steam at the turbine exit increases. This side effect can be corrected by reheating the steam.



3- THE REHEAT CYCLE

The efficiency of the Rankine cycle could be increased by increasing the pressure during the addition of heat. However, the increase in pressure also increases the moisture content of the steam in the low-pressure end of the turbine. The reheat cycle has been developed to take advantage of the increased efficiency with higher pressures and yet avoid excessive moisture in the low-pressure stages of the turbine. This cycle is shown schematically and on a T-s diagram in Fig. 1. The unique feature of this cycle is that the steam is expanded to some intermediate pressure in the turbine and is then reheated in the boiler, after which it expands in the turbine to the exhaust pressure. It is evident from the T-s diagram that there is very little gain in efficiency from reheating the steam, because the average temperature at which heat is supplied is not greatly changed. The chief advantage is in decreasing to a safe value the moisture content in the low-pressure stages of the turbine.

FIGURE 1
The ideal reheat cycle



Ex1- Consider a reheat cycle utilizing steam. Steam leaves the boiler and enters the turbine at 4 MPa, 400°C. After expansion in the turbine to 400 kPa, the steam is reheated to 400°C and then expanded in the low-pressure turbine to 10 kPa. Determine the cycle efficiency. For each control volume analyzed, the thermodynamic model is the steam tables, the process is steady state, and changes in kinetic and potential energies are negligible.

Ans.

For the high-pressure turbine,

Control volume: High-pressure turbine.

Inlet state: P_3, T_3 known; state fixed.

Exit state: P_4 known.

Analysis

$$\text{Energy Eq.: } w_{h-p} = h_3 - h_4$$

$$\text{Entropy Eq.: } s_3 = s_4$$

Solution

Substituting,

$$h_3 = 3213.6, \quad s_3 = 6.7690$$

$$s_4 = s_3 = 6.7690 = 1.7766 + x_4 5.1193, \quad x_4 = 0.9752$$

$$h_4 = 604.7 + 0.9752(2133.8) = 2685.6 \text{ kJ/kg}$$

For the low-pressure turbine,

Control volume: Low-pressure turbine.

Inlet state: P_5, T_5 known; state fixed.

Exit state: P_6 known.

Analysis

$$\text{Energy Eq.: } w_{l-p} = h_5 - h_6$$

$$\text{Entropy Eq.: } s_5 = s_6$$

Solution

Upon substituting,

$$h_5 = 3273.4 \text{ kJ/kg} \quad s_5 = 7.8985 \text{ kJ/kg K}$$

$$s_6 = s_5 = 7.8985 = 0.6493 + x_6 7.5009, \quad x_6 = 0.9664$$

$$h_6 = 191.8 + 0.9664(2392.8) = 2504.3 \text{ kJ/kg}$$

For the overall turbine, the total work output w_t is the sum of w_{h-p} and w_{l-p} , so that

$$\begin{aligned} w_t &= (h_3 - h_4) + (h_5 - h_6) \\ &= (3213.6 - 2685.6) + (3273.4 - 2504.3) \\ &= 1297.1 \text{ kJ/kg} \end{aligned}$$

For the pump,

Control volume: Pump.

Inlet state: P_1 known, saturated liquid; state fixed.

Exit state: P_2 known.

Analysis

$$\text{Energy Eq.: } w_p = h_2 - h_1$$

$$\text{Entropy Eq.: } s_2 = s_1$$

Since $s_2 = s_1$,

$$h_2 - h_1 = \int_1^2 v \, dP = v(P_2 - P_1)$$

Solution

Substituting,

$$w_p = v(P_2 - P_1) = (0.00101)(4000 - 10) = 4.0 \text{ kJ/kg}$$

$$h_2 = 191.8 + 4.0 = 195.8 \text{ kJ/kg}$$

Finally, for the boiler

Control volume: Boiler.

Inlet states: States 2 and 4 both known (above).

Exit states: States 3 and 5 both known (as given).

Analysis

$$\text{Energy Eq.: } q_H = (h_3 - h_2) + (h_5 - h_4)$$

Solution

Substituting,

$$q_H = (h_3 - h_2) + (h_5 - h_4) \\ = (3213.6 - 195.8) + (3273.4 - 2685.6) = 3605.6 \text{ kJ/kg}$$

Therefore,

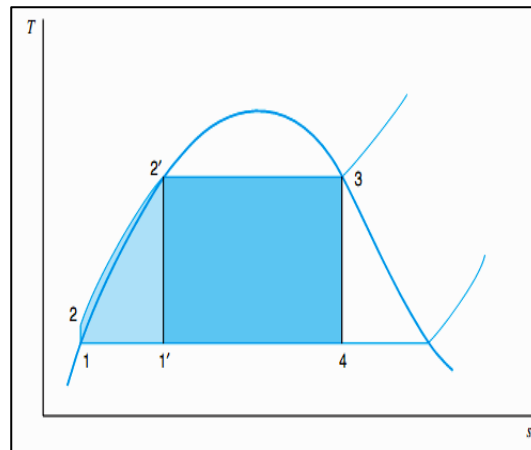
$$w_{\text{net}} = w_t - w_p = 1297.1 - 4.0 = 1293.1 \text{ kJ/kg}$$

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_H} = \frac{1293.1}{3605.6} = 35.9\%$$

4- THE REGENERATIVE CYCLE AND FEEDWATER HEATERS

Another important variation from the Rankine cycle is the regenerative cycle, which uses feed water heaters. The basic concepts of this cycle can be demonstrated by considering the Rankine cycle without superheat, as shown in Fig. 2. During the process between states 2 and 2', the working fluid is heated while in the liquid phase, and the average temperature of the working fluid is much lower than during the vaporization process 2'-3. The process between states 2 and 2' causes the average temperature at which heat is supplied in the Rankine cycle to be lower than in the Carnot cycle $1'-2'-3-4-1'$; efficiency of the Rankine cycle is lower than that of the corresponding Carnot cycle. In the regenerative cycle the working fluid enters the boiler at some state between 2 and 2'; consequently, the average temperature at which heat is supplied is higher.

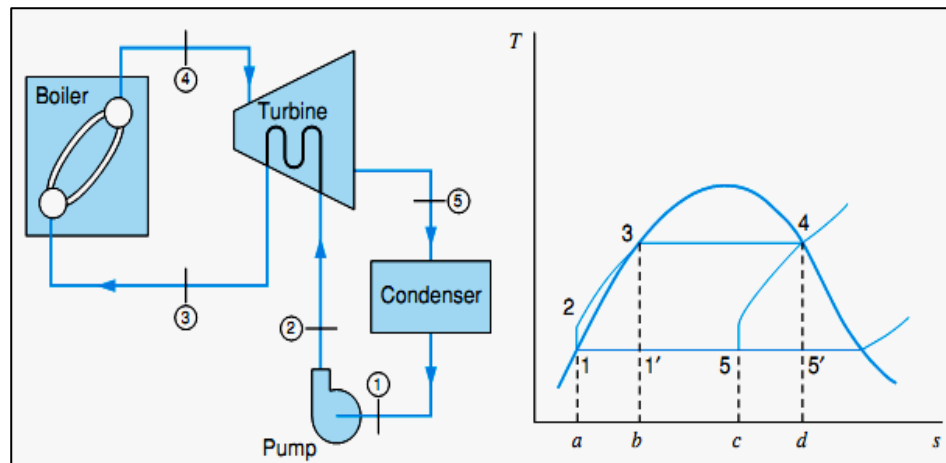
FIGURE 2 T-s diagram showing the relationships between Carnot-cycle efficiency and Rankine-cycle efficiency.



Consider first an idealized regenerative cycle, as shown in Fig. 3. The unique feature of this cycle compared to the Rankine cycle is that after leaving the pump, the liquid circulates around the turbine casing, counterflow to the direction of vapor flowing through the turbine. Thus, it is possible to transfer to the liquid flowing around the turbine the heat from the vapor as it flows through the turbine. Let us assume for the moment that this is a reversible heat transfer; that is, at each point the temperature of the vapor is only infinitesimally higher than the temperature of the liquid. In this instance, line 4-5 on the T-s diagram of Fig. 3, which represents the states of the vapor flowing through the turbine, is exactly parallel to line 1-2-3, which represents the pumping process (1-2)

and the states of the liquid flowing around the turbine. Consequently, areas 2–3–b–a–2 and 5–4–d–c–5 are not only equal but congruous, and these areas, respectively, represent the heat transferred to the liquid and from the vapor. Heat is also transferred to the working fluid at constant temperature in process 3–4, and area 3–4–d–b–3 represents this heat transfer. Heat is transferred from the working fluid in process 5–1, and area 1–5–c–a–1 represents this heat transfer. This area is exactly equal to area 1'–5'–d–b–1', which is the heat rejected in the related Carnot cycle 1'–3–4–5'–1'. Thus, the efficiency of this idealized regenerative cycle is exactly equal to the efficiency of the Carnot cycle with the same heat supply and heat rejection temperatures.

FIGURE 3 The ideal regenerative cycle.

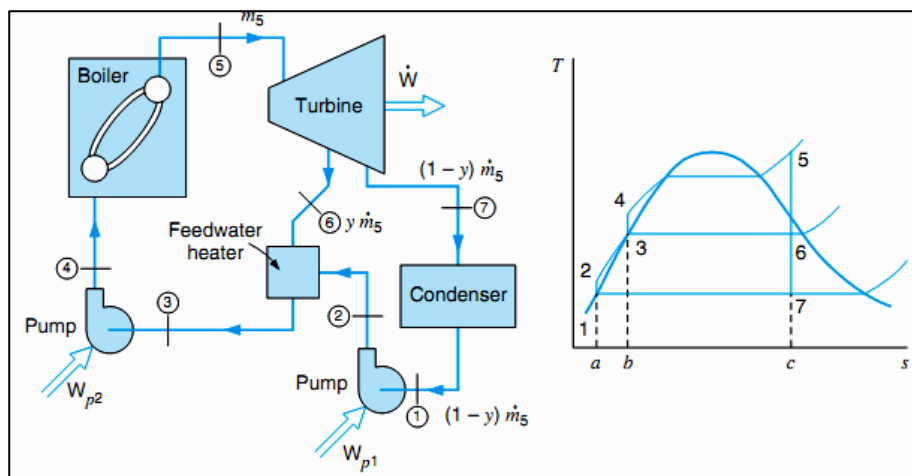


The practical regenerative cycle extracts some of the vapor after it has partially expanded in the turbine and uses feedwater heaters (FWH), as shown in Fig. 4. Steam enters the turbine at state 5. After expansion to state 6, some of the steam is extracted and enters the FWH. The steam that is not extracted is expanded in the turbine to state 7 and is then condensed in the condenser. This condensate is pumped into the FWH, where it mixes with the steam extracted from the turbine. The proportion of steam extracted is just sufficient to cause the liquid leaving the FWH to be saturated at state 3. Note that the liquid has not been pumped to the boiler pressure, but only to the intermediate pressure corresponding to state 6. Another pump is required to pump the liquid leaving the FWH boiler pressure. The significant point is that the average temperature at which heat is supplied has been increased.

Consider a control volume around the open FWH in Fig. 4. The conservation of mass requires

$$\dot{m}_2 + \dot{m}_6 = \dot{m}_3$$

FIGURE 4
Regenerative cycle
with an open FWH



satisfied with the extraction fraction as

$$y = \dot{m}_6 / \dot{m}_5$$

so

$$\dot{m}_7 = (1 - y)\dot{m}_5 = \dot{m}_1 = \dot{m}_2$$

The energy equation with no external heat transfer and no work becomes

$$\dot{m}_2 h_2 + \dot{m}_6 h_6 = \dot{m}_3 h_3$$

into which we substitute the mass flow rates ($\dot{m}_3 = \dot{m}_5$) as

$$(1 - y)\dot{m}_5 h_2 + y\dot{m}_5 h_6 = \dot{m}_5 h_3$$

We take state 3 as the limit of saturated liquid (we do not want to heat it further, as it would move into the two-phase region and damage the pump P2) and then solve for y :

$$y = \frac{h_3 - h_2}{h_6 - h_2}$$

Ex2- Consider a regenerative cycle using steam as the working fluid. Steam leaves the boiler and enters the turbine at 4 MPa, 400°C. After expansion to 400 kPa, some of the steam is extracted from the turbine to heat the feedwater in an open FWH. The pressure in the FWH is 400 kPa, and the water leaving it is saturated liquid at 400 kPa. The steam not extracted expands to 10 kPa. Determine the cycle efficiency.

Ans.

For the low-pressure pump,

Control volume: Low-pressure pump.

Inlet state: P_1 known, saturated liquid; state fixed.

Exit state: P_2 known.

Analysis

$$\text{Energy Eq.: } w_{p1} = h_2 - h_1$$

$$\text{Entropy Eq.: } s_2 = s_1$$

Therefore,

$$h_2 - h_1 = \int_1^2 v \, dP = v(P_2 - P_1)$$

Solution

Substituting,

$$w_{p1} = v(P_2 - P_1) = (0.00101)(400 - 10) = 0.4 \text{ kJ/kg}$$

$$h_2 = h_1 + w_p = 191.8 + 0.4 = 192.2 \text{ kJ/kg}$$

For the turbine,

Control volume: Turbine.*Inlet state:* P_5, T_5 known; state fixed.*Exit state:* P_6 known; P_7 known.**Analysis**

$$\text{Energy Eq.: } w_t = (h_5 - h_6) + (1 - y)(h_6 - h_7)$$

$$\text{Entropy Eq.: } s_5 = s_6 = s_7$$

For the FWH,

Control volume: FWH.*Inlet states:* States 2 and 6 both known (as given).*Exit state:* P_3 known, saturated liquid; state fixed.**Analysis**

$$\text{Energy Eq.: } y(h_6) + (1 - y)h_2 = h_3$$

Solution

After substitution,

$$y(2685.6) + (1 - y)(192.2) = 604.7$$

$$y = 0.1654$$

We can now calculate the turbine work.

$$\begin{aligned} w_t &= (h_5 - h_6) + (1 - y)(h_6 - h_7) \\ &= (3213.6 - 2685.6) + (1 - 0.1654)(2685.6 - 2144.1) \\ &= 979.9 \text{ kJ/kg} \end{aligned}$$

For the high-pressure pump,

Control volume: High-pressure pump.*Inlet state:* State 3 known (as given).*Exit state:* P_4 known.**Analysis**

$$\text{Energy Eq.: } w_{p2} = h_4 - h_3$$

$$\text{Entropy Eq.: } s_4 = s_3$$

Solution

Substituting,

$$w_{p2} = v(P_4 - P_3) = (0.001084)(4000 - 400) = 3.9 \text{ kJ/kg}$$

$$h_4 = h_3 + w_{p2} = 604.7 + 3.9 = 608.6 \text{ kJ/kg}$$

Therefore,

$$\begin{aligned} w_{\text{net}} &= w_t - (1 - y)w_{p1} - w_{p2} \\ &= 979.9 - (1 - 0.1654)(0.4) - 3.9 = 975.7 \text{ kJ/kg} \end{aligned}$$

Finally, for the boiler,

Control volume: Boiler.*Inlet state:* P_4, h_4 known (as given); state fixed.*Exit state:* State 5 known (as given).

Analysis

$$\text{Energy Eq.: } q_H = h_5 - h_4$$

Solution

Substituting,

$$q_H = h_5 - h_4 = 3213.6 - 608.6 = 2605.0 \text{ kJ/kg}$$

$$\eta_{th} = \frac{w_{net}}{q_H} = \frac{975.7}{2605.0} = 37.5\%$$

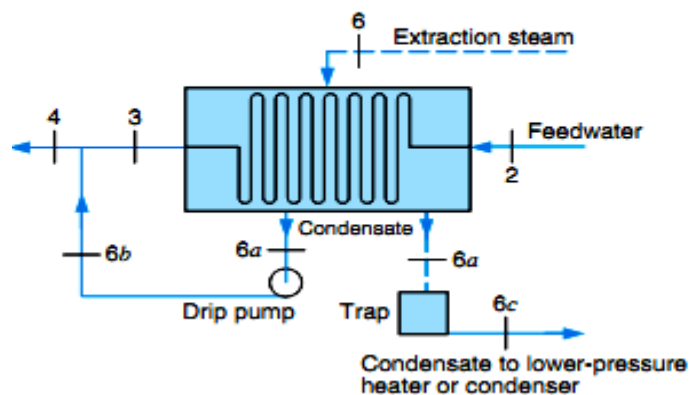
Another frequently used type of FWH, known as a closed feedwater heater, is one in which the steam and feedwater do not mix. Rather, heat is transferred from the extracted steam as it condenses on the outside of tubes while the feedwater flows through the tubes. In a closed heater, a schematic sketch of which is shown in Fig. 5, the steam and feedwater may be at considerably different pressures. The condensate may be pumped into the feedwater line, or it may be removed through a trap to a lower-pressure heater or to the condenser. (A trap is a device that permits liquid but not vapor to flow to a region of lower pressure.). Let us analyze the closed FWH in Fig.5, when a trap with a drain to the condenser is used. Assume that can heat the feedwater up to the temperature of the condensing extraction flow, that is, $T_3 = T_4 = T_{6a}$, as there is no drip pump. Conservation of mass for the feedwater heater is:-

$$\dot{m}_4 = \dot{m}_3 = \dot{m}_2 = \dot{m}_5; \quad \dot{m}_6 = y\dot{m}_5 = \dot{m}_{6a} = \dot{m}_{6c}$$

Notice that the extraction flow is added to the condenser, so the flow rate at state 2 is the same as at state 5. The energy equation is

$$\dot{m}_5 h_2 + y\dot{m}_5 h_6 = \dot{m}_5 h_3 + y\dot{m}_5 h_{6a}$$

FIGURE 5
Schematic arrangement
for a closed FWH



which we can solve for y as

$$y = \frac{h_3 - h_2}{h_6 - h_{6a}}$$

Open FWHs have the advantages of being less expensive and having better heat-transfer characteristics than closed FWHs. They have the disadvantage of requiring a pump to handle the feedwater between each heater.

A typical arrangement of the main components in an actual power plant is shown in Fig. 6. Note that one open FWH is a deaerating FWH; this heater has the dual purpose of heating and removing the air from the feedwater. Unless the air is removed, excessive corrosion occurs in the boiler. Note also that the condensate from the high-pressure heater drains (through a trap) to the intermediate heater, and the condensate from the intermediate heater drains to the deaerating FWH. The condensate from the low-pressure heater drains to the condenser. Many actual power plants combine one reheat stage with a number of extraction stages. The principles already considered are readily applied to such a cycle.

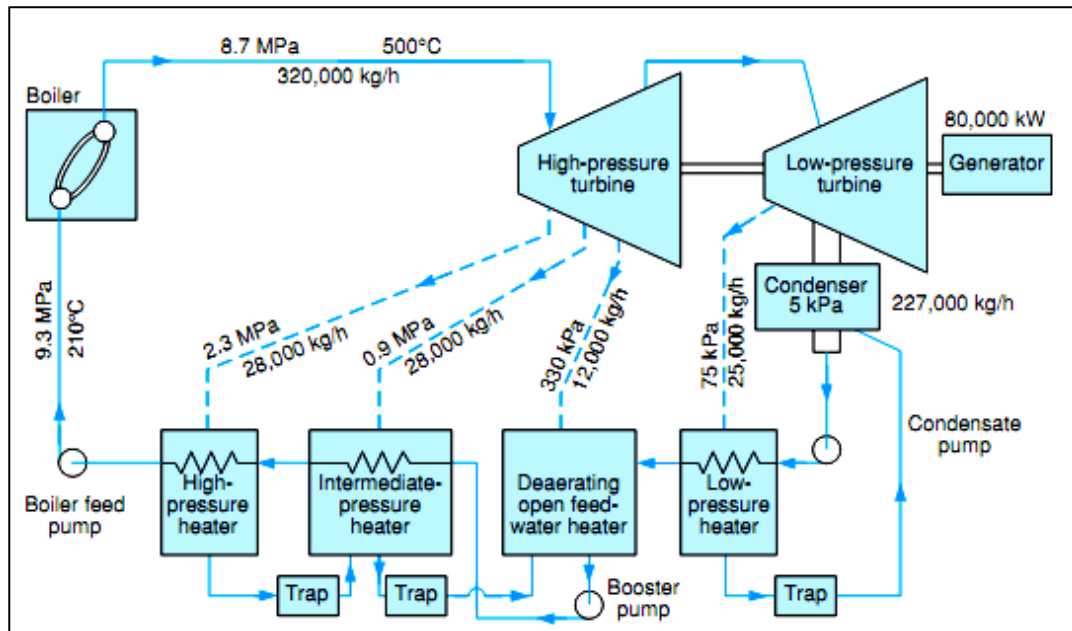


FIGURE 5, Arrangement of heaters in an actual power plant utilizing regenerative FWHs

GAS POWER CYCLES

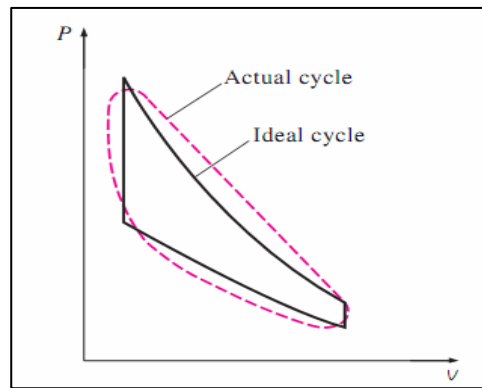
The devices or systems used to produce a net power output are often called engines, and the thermodynamic cycles they operate on are called power cycles. The devices or systems used to produce a refrigeration effect are called refrigerators, air conditioners, or heat pumps, and the cycles they operate on are called refrigeration cycles.

1 -BASIC CONSIDERATIONS IN THE ANALYSIS OF POWER CYCLES

The cycles encountered in actual devices are difficult to analyze because of the presence of complicating effects, such as friction, and the absence of sufficient time for establishment of the equilibrium conditions during the cycle.

When the actual cycle is stripped of all the internal irreversibilities and complexities, we end up with a cycle that resembles the actual cycle closely but is made up totally of internally reversible processes. Such a cycle is called an ideal cycle (Fig.1).

FIG.1
The analysis of many complex processes can be reduced to a manageable level by utilizing some idealizations



The conclusions reached from the analysis of ideal cycles are also applicable to actual cycles. The thermal efficiency of the Otto cycle, the ideal cycle for spark-ignition automobile engines, for example, increases with the compression ratio. This is also the case for actual automobile engines.

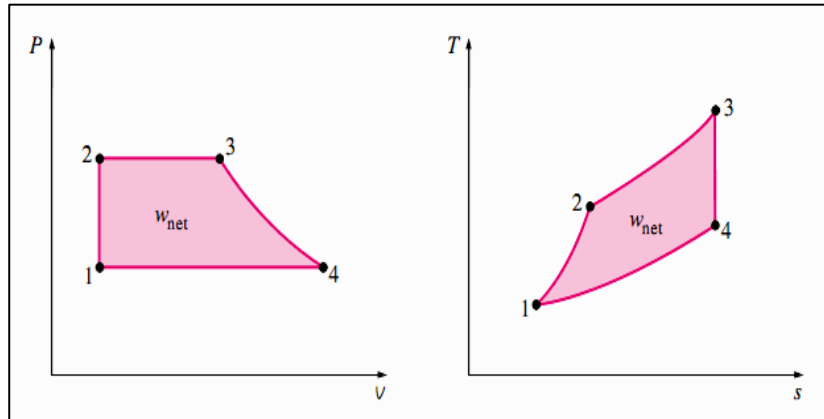
Heat engines are designed for the purpose of converting thermal energy to work, and their performance is expressed in terms of the thermal efficiency η_{th} , which is the ratio of the net work produced by the engine to the total heat input:

$$\eta_{th} = \frac{W_{net}}{Q_{in}} \quad \text{or} \quad \eta_{th} = \frac{w_{net}}{q_{in}}$$

The property diagrams such as the P-v and T-s diagrams have served as valuable aids in the analysis of thermodynamic processes. On both the P-v and T-s diagrams, the area enclosed by the process curves of a cycle represents the net work produced during the cycle (Fig. 2), which is also equivalent to the net heat transfer for that cycle.

FIGURE 2

On both P-v and T-s diagrams, the area enclosed by the process curve represents the net work of the cycle



The area under the process curve on a T-s diagram represents the heat transfer for that process. The area under the heat addition process on a T-s diagram is a geometric measure of the total heat supplied during the cycle q_{in} , and the area under the heat rejection process is a measure of the total heat rejected q_{out} . The difference between these two (the area enclosed by the cyclic curve) is the net heat transfer, which is also the net work produced during the cycle. Therefore, on a T-s diagram, the ratio of the area enclosed by the cyclic curve to the area under the heat-addition process curve represents the thermal efficiency of the cycle. *Any modification that increases the ratio of these two areas will also increase the thermal efficiency of the cycle.*

2 -THE CARNOT CYCLE AND ITS VALUE IN ENGINEERING

The Carnot cycle is composed of four totally reversible processes: isothermal heat addition, isentropic expansion, isothermal heat rejection, and isentropic compression. The P-v and T-s diagrams of a Carnot cycle are replotted in Fig. 3. The Carnot cycle can be executed in a closed system (a piston–cylinder device) or a steady-flow system (utilizing two turbines and two compressors, as shown in Fig. 4), and either a gas or a vapor can be utilized as the working fluid. The Carnot cycle is the most efficient cycle that can be executed between a heat source at temperature T_H and a sink at temperature T_L , and its thermal efficiency is expressed as

$$\eta_{th,Carnot} = 1 - \frac{T_L}{T_H}$$

FIGURE 3

P-v and T-s diagrams of a Carnot cycle.

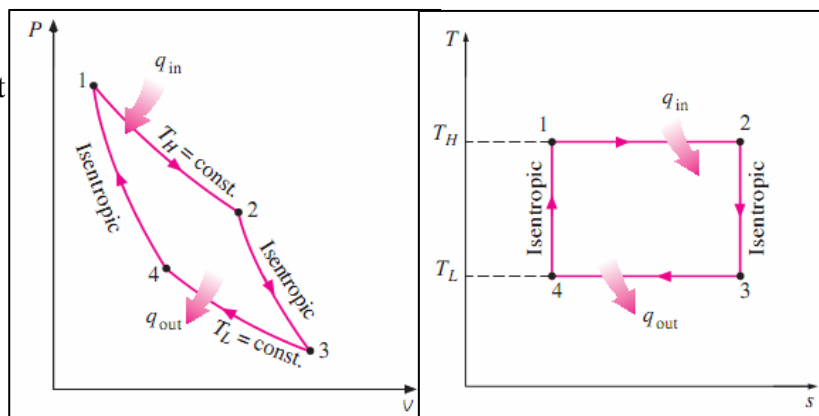
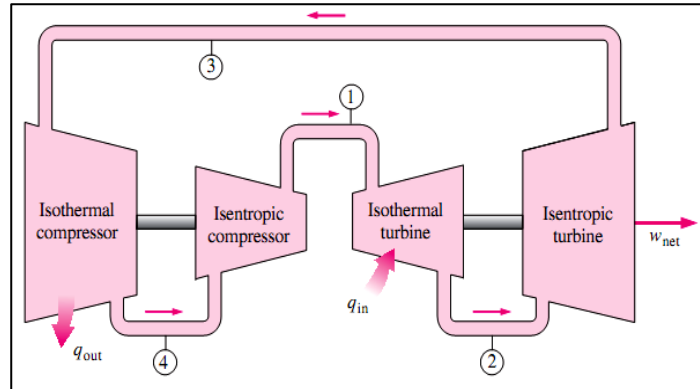


FIGURE 4
A steady-flow Carnot engine.



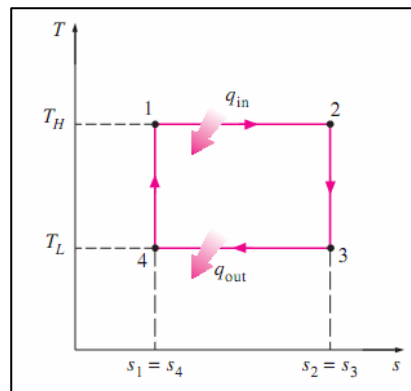
**Thermal efficiency increases with an increase in the average temperature at which heat is supplied to the system or with a decrease in the average temperature at which heat is rejected from the system*

Ex.1 Show that the thermal efficiency of a Carnot cycle operating between the temperature limits of T_H and T_L is solely a function of these two temperatures and is give

Analysis The T-s diagram of a Carnot cycle is redrawn in Fig. All four processes that comprise the Carnot cycle are reversible, and thus the area under each process curve represents the heat transfer for that process. Heat is transferred to the system during process 1-2 and rejected during process 3-4. Therefore, the amount of heat input and heat output for the cycle can be expressed as

$$q_{in} = T_H(s_2 - s_1) \quad \text{and} \quad q_{out} = T_L(s_3 - s_4) = T_L(s_2 - s_1)$$

$$\eta_{th} = \frac{w_{net}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}} = 1 - \frac{T_L(s_2 - s_1)}{T_H(s_2 - s_1)} = 1 - \frac{T_L}{T_H}$$



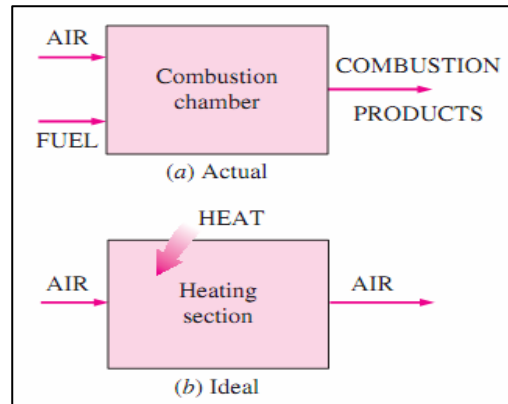
3 - AIR-STANDARD ASSUMPTIONS

In gas power cycles, the working fluid remains a gas throughout the entire cycle. Spark-ignition engines, diesel engines, and conventional gas turbines are familiar examples of devices that operate on gas cycles. The actual gas power cycles are rather complex. To reduce the analysis to a manageable level, we utilize the following approximations, commonly known as the air-standard assumptions:

1. The working fluid is air, which continuously circulates in a closed loop and always behaves as an ideal gas.
2. All the processes that make up the cycle are internally reversible.
3. The combustion process is replaced by a heat-addition process from an external source (Fig.5).
4. The exhaust process is replaced by a heat-rejection process that restores the working fluid to its initial state.

FIGURE 5

The combustion process is replaced by a heat-addition process in ideal cycles.



4 - AN OVERVIEW OF RECIPROCATING ENGINES

Despite its simplicity, the reciprocating engine (basically a piston–cylinder device) is one of the rare inventions that has proved to be very versatile and to have a wide range of applications.

The basic components of a reciprocating engine are shown in Fig. 6. The piston reciprocates in the cylinder between two fixed positions called the **top dead center (TDC)** the position of the piston when it forms the smallest volume in the cylinder and the **bottom dead center (BDC)** the position of the piston when it forms the largest volume in the cylinder. The distance between the TDC and the BDC is the largest distance that the piston can travel in one direction, and it is called the **stroke** of the engine. The diameter of the piston is called the **bore**. The air or air–fuel mixture is drawn into the cylinder through the intake valve, and the combustion products are expelled from the cylinder through the exhaust valve. The minimum volume formed in the cylinder when the piston is at TDC is called the **clearance volume** (Fig. 7). The volume displaced by the piston as it moves between TDC and BDC is called the displacement volume. The ratio of the maximum volume formed in the cylinder to the minimum (clearance) volume is called the **compression ratio r** of the engine:

$$r = \frac{V_{\max}}{V_{\min}} = \frac{V_{\text{BDC}}}{V_{\text{TDC}}}$$

FIGURE 6
Nomenclature for reciprocating engines

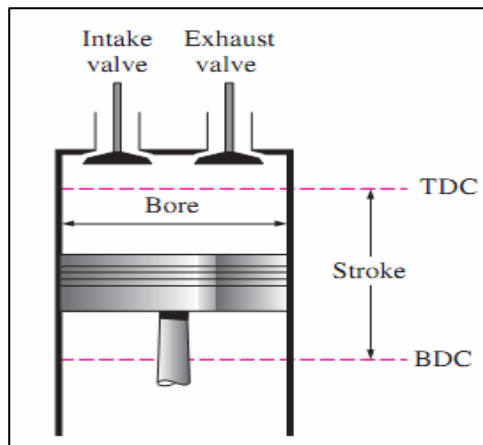
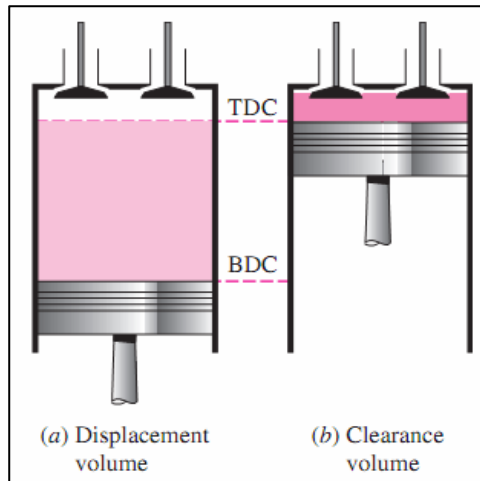


FIGURE 7
Displacement and clearance volumes of a reciprocating engine



Another term frequently used in conjunction with reciprocating engines is the **mean effective pressure (MEP)**. It is a fictitious pressure that, if it acted on the piston during the entire power stroke, would produce the same amount of net work as that produced during the actual cycle (Fig. 8). That is,

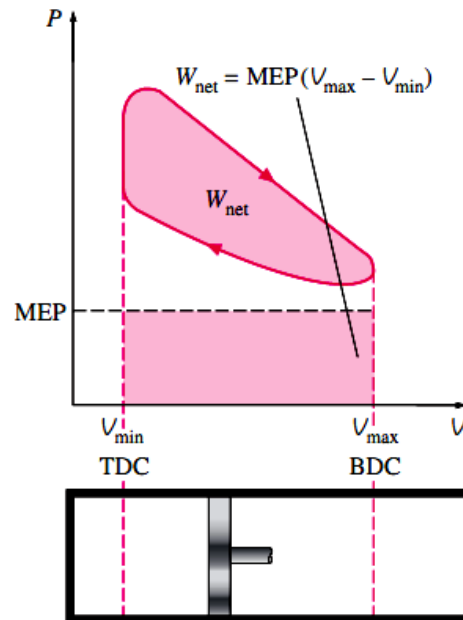
$$W_{\text{net}} = \text{MEP} \times \text{Piston area} \times \text{Stroke} = \text{MEP} \times \text{Displacement volume}$$

or

$$\text{MEP} = \frac{W_{\text{net}}}{V_{\text{max}} - V_{\text{min}}} = \frac{w_{\text{net}}}{v_{\text{max}} - v_{\text{min}}} \quad (\text{kPa})$$

The mean effective pressure can be used as a parameter to compare the performances of reciprocating engines of equal size. The engine with a larger value of MEP delivers more net work per cycle and thus performs better.

FIGURE 8
The net work output of a cycle is equivalent to the product of the mean effective pressure and the displacement volume.



5 -OTTO CYCLE: THE IDEAL CYCLE FOR SPARK-IGNITION ENGINES

The Otto cycle is the ideal cycle for spark-ignition reciprocating engines. In most spark-ignition engines, the piston executes four complete strokes (two mechanical cycles) within the cylinder, and the crankshaft completes two revolutions for each thermodynamic cycle. These engines are called four-stroke internal combustion engines. A schematic of each stroke as well as a P-v diagram for an actual four-stroke spark-ignition engine is given in Fig. 9(a).

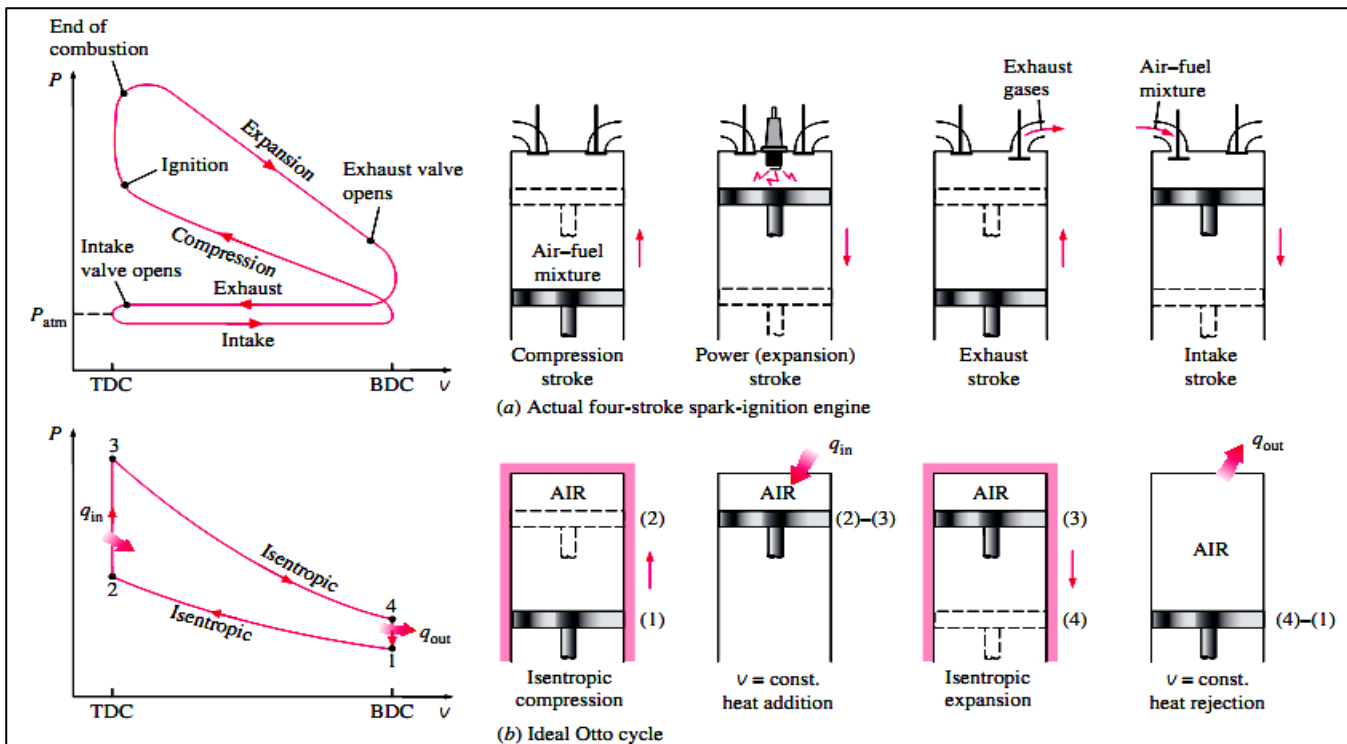


FIGURE 9 Actual and ideal cycles in spark-ignition engines and their P-v diagrams.

The ideal Otto cycle. It consists of four internally reversible processes:

1-2 Isentropic compression

2-3 Constant-volume heat addition

3-4 Isentropic expansion

4-1 Constant-volume heat rejection

The execution of the Otto cycle in a piston–cylinder device together with a P-v diagram is illustrated in Fig. 9b. The T-s diagram of the Otto cycle is given in Fig. 10

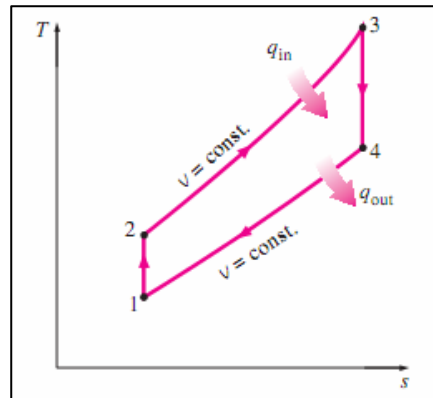


FIGURE 10

T-s diagram of the ideal Otto cycle.

The Otto cycle is executed in a closed system, and disregarding the changes in kinetic and potential energies, the energy balance for any of the processes is expressed, on a unit-mass basis, as

$$(q_{\text{in}} - q_{\text{out}}) + (w_{\text{in}} - w_{\text{out}}) = \Delta u \quad (\text{kJ/kg})$$

No work is involved during the two heat transfer processes since both take place at constant volume. Therefore, heat transfer to and from the working fluid can be expressed as

$$q_{\text{in}} = u_3 - u_2 = c_v(T_3 - T_2)$$

and

$$q_{\text{out}} = u_4 - u_1 = c_v(T_4 - T_1)$$

Then the thermal efficiency of the ideal Otto cycle under the cold air standard assumptions becomes

$$\eta_{\text{th, Otto}} = \frac{w_{\text{net}}}{q_{\text{in}}} = 1 - \frac{q_{\text{out}}}{q_{\text{in}}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_1(T_4/T_1 - 1)}{T_2(T_3/T_2 - 1)}$$

Processes 1-2 and 3-4 are isentropic, and $v_2 = v_3$ and $v_4 = v_1$. Thus,

$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{k-1} = \left(\frac{v_3}{v_4}\right)^{k-1} = \frac{T_4}{T_3}$$

Substituting these equations into the thermal efficiency relation and simplifying give

$$\eta_{\text{th, Otto}} = 1 - \frac{1}{r^{k-1}}$$

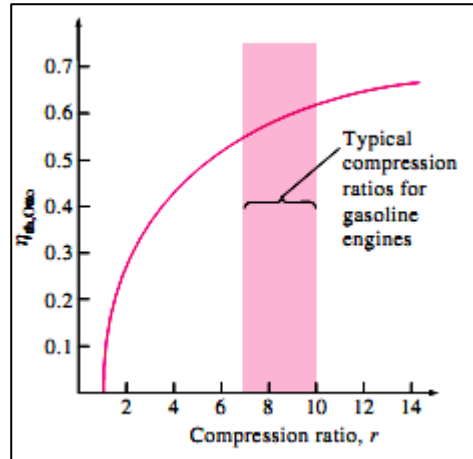
where

$$r = \frac{V_{\text{max}}}{V_{\text{min}}} = \frac{v_1}{v_2} = \frac{v_1}{v_2}$$

is the **compression ratio** and k is the specific heat ratio c_p/c_v .

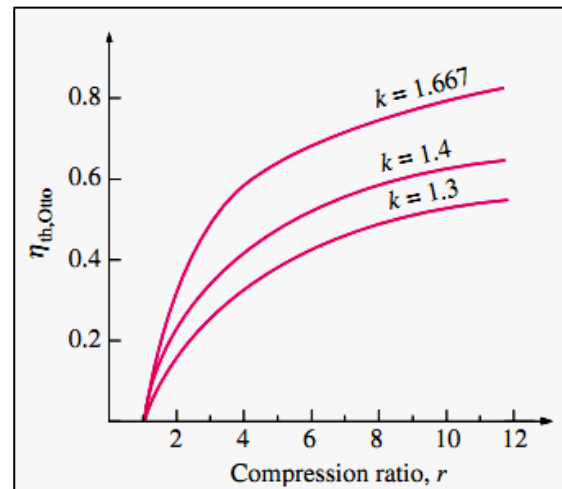
A plot of thermal efficiency versus the compression ratio is given in Fig.11 for $k = 1.4$, which is the specific heat ratio value of air at room temperature. For a given compression ratio, the thermal efficiency of an actual spark-ignition engine is less than that of an ideal Otto cycle because of the irreversibilities, such as friction, and other factors such as incomplete combustion.

FIGURE 11
Thermal efficiency of the ideal Otto cycle as a function of compression ratio ($k = 1.4$)



The second parameter affecting the thermal efficiency of an ideal Otto cycle is the specific heat ratio k . For a given compression ratio, an ideal Otto cycle using a monatomic gas (such as argon or helium, $k = 1.667$) as the working fluid will have the highest thermal efficiency. The specific heat ratio k , and thus the thermal efficiency of the ideal Otto cycle, decreases as the molecules of the working fluid get larger (Fig.12). At room temperature it is 1.4 for air, 1.3 for carbon dioxide, and 1.2 for ethane.

FIGURE 12
The thermal efficiency of the Otto cycle increases with the specific heat ratio k of the working fluid.



Ex.2-An ideal Otto cycle has a compression ratio of 8. At the beginning of the compression process, air is at 100 kPa and 17°C, and 800 kJ/kg of heat is transferred to air during the constant-volume heat-addition process. Accounting for the variation of specific heats of air with temperature, determine

- (a) the maximum temperature and pressure that occur during the cycle,
 (b) the net work output, (c) the thermal efficiency, and (d) the mean effective pressure for the cycle.

Ans.

Analysis The P-v diagram of the ideal Otto cycle described is shown in Fig. the air contained in the cylinder forms a closed system.

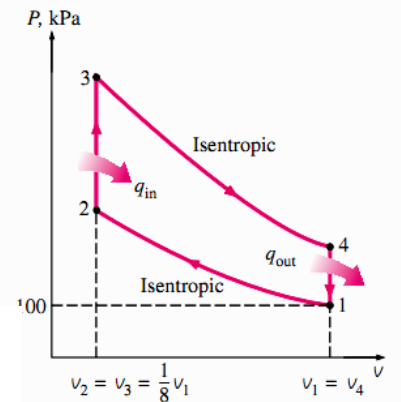
a-The maximum temperature and pressure in an

Otto cycle occur at the end of the constant-volume heat-addition process (state 3). But first to determine the temperature and pressure of air at the end of the isentropic compression process (state 2), using data from

Table A-17:

$$T_1 = 290 \text{ K} \rightarrow u_1 = 206.91 \text{ kJ/kg}$$

$$v_{r1} = 676.1$$



Process 1-2 (isentropic compression of an ideal gas):

$$\frac{v_{r2}}{v_{r1}} = \frac{v_2}{v_1} = \frac{1}{r} \rightarrow v_{r2} = \frac{v_{r1}}{r} = \frac{676.1}{8} = 84.51 \rightarrow T_2 = 652.4 \text{ K}$$

$$u_2 = 475.11 \text{ kJ/kg}$$

$$\frac{P_2 v_2}{T_2} = \frac{P_1 v_1}{T_1} \rightarrow P_2 = P_1 \left(\frac{T_2}{T_1} \right) \left(\frac{v_1}{v_2} \right)$$

$$= (100 \text{ kPa}) \left(\frac{652.4 \text{ K}}{290 \text{ K}} \right) (8) = 1799.7 \text{ kPa}$$

Process 2-3 (constant-volume heat addition):

$$q_{in} = u_3 - u_2$$

$$800 \text{ kJ/kg} = u_3 - 475.11 \text{ kJ/kg}$$

$$u_3 = 1275.11 \text{ kJ/kg} \rightarrow T_3 = 1575.1 \text{ K}$$

$$v_{r3} = 6.108$$

$$\frac{P_3 v_3}{T_3} = \frac{P_2 v_2}{T_2} \rightarrow P_3 = P_2 \left(\frac{T_3}{T_2} \right) \left(\frac{v_2}{v_3} \right)$$

$$= (1.7997 \text{ MPa}) \left(\frac{1575.1 \text{ K}}{652.4 \text{ K}} \right) (1) = 4.345 \text{ MPa}$$

(b) The net work output for the cycle is determined either by finding the boundary ($P dV$) work involved in each process by integration and adding them or by finding the net heat transfer that is equivalent to the net work done during the cycle. We take the latter approach. However, first we need to find the internal energy of the air at state 4:

Process 3-4 (isentropic expansion of an ideal gas):

$$\frac{v_{r4}}{v_{r3}} = \frac{v_4}{v_3} = r \rightarrow v_{r4} = r v_{r3} = (8)(6.108) = 48.864 \rightarrow T_4 = 795.6 \text{ K}$$

$$u_4 = 588.74 \text{ kJ/kg}$$

Process 4-1 (constant-volume heat rejection):

$$-q_{\text{out}} = u_1 - u_4 \rightarrow q_{\text{out}} = u_4 - u_1$$

$$q_{\text{out}} = 588.74 - 206.91 = 381.83 \text{ kJ/kg}$$

Thus,

$$w_{\text{net}} = q_{\text{net}} = q_{\text{in}} - q_{\text{out}} = 800 - 381.83 = \mathbf{418.17 \text{ kJ/kg}}$$

(c) The thermal efficiency of the cycle is determined from its definition:

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{418.17 \text{ kJ/kg}}{800 \text{ kJ/kg}} = \mathbf{0.523 \text{ or } 52.3\%}$$

Under the cold-air-standard assumptions (constant specific heat values at room temperature), the thermal efficiency would be (Eq. 9-8)

$$\eta_{\text{th, Otto}} = 1 - \frac{1}{r^{k-1}} = 1 - r^{1-k} = 1 - (8)^{1-1.4} = 0.565 \text{ or } 56.5\%$$

which is considerably different from the value obtained above. Therefore, care should be exercised in utilizing the cold-air-standard assumptions.

(d) The mean effective pressure is determined from its definition

$$\text{MEP} = \frac{w_{\text{net}}}{v_1 - v_2} = \frac{w_{\text{net}}}{v_1 - v_1/r} = \frac{w_{\text{net}}}{v_1(1 - 1/r)}$$

where

$$v_1 = \frac{RT_1}{P_1} = \frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(290 \text{ K})}{100 \text{ kPa}} = 0.832 \text{ m}^3/\text{kg}$$

Thus,

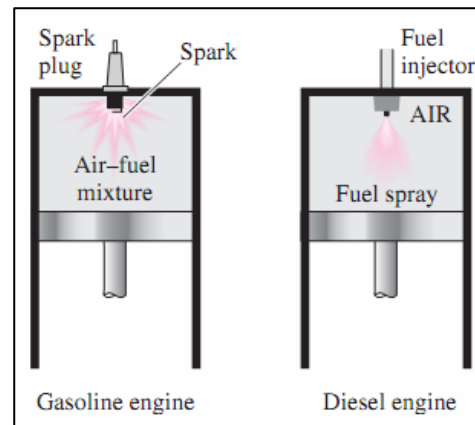
$$\text{MEP} = \frac{418.17 \text{ kJ/kg}}{(0.832 \text{ m}^3/\text{kg})(1 - \frac{1}{8})} \left(\frac{1 \text{ kPa} \cdot \text{m}^3}{1 \text{ kJ}} \right) = \mathbf{574 \text{ kPa}}$$

6 -DIESEL CYCLE: THE IDEAL CYCLE FOR COMPRESSION IGNITION ENGINES

The Diesel cycle is the ideal cycle for CI reciprocating engines. In spark-ignition engines (also known as gasoline engines), the air–fuel mixture is compressed to a temperature that is below the auto-ignition temperature of the fuel, and the combustion process is initiated by firing a spark plug. In CI engines (also known as diesel engines), the air is compressed to a temperature that is above the auto-ignition temperature of the fuel, and combustion starts on contact as the fuel is injected into this hot air. Therefore, the spark plug and carburetor are replaced by a fuel injector in diesel engines (Fig.13).

FIGURE 13

In diesel engines, the spark plug is replaced by a fuel injector, and only air is compressed during the compression process.



The fuel injection process in diesel engines starts when the piston approaches TDC and continues during the first part of the power stroke. Therefore, the combustion process in these engines takes place over a longer interval. Because of this longer duration, the combustion process in the ideal Diesel cycle is approximated as a constant-pressure heat-addition process. In fact, this is the only process where the Otto and the Diesel cycles differ. The remaining three processes are the same for both ideal cycles. That is, process 1-2 is isentropic compression, 3-4 is isentropic expansion, and 4-1 is constant-volume heat rejection. The similarity between the two cycles is also apparent from the P-v and T-s diagrams of the Diesel cycle, shown in Fig. 14.

Noting that the Diesel cycle is executed in a piston–cylinder device, which forms a closed system, the amount of heat transferred to the working fluid at constant pressure and rejected from it at constant volume can be expressed as

$$\begin{aligned} q_{\text{in}} - w_{b,\text{out}} &= u_3 - u_2 \rightarrow q_{\text{in}} = P_2(v_3 - v_2) + (u_3 - u_2) \\ &= h_3 - h_2 = c_p(T_3 - T_2) \end{aligned}$$

and

$$-q_{\text{out}} = u_1 - u_4 \rightarrow q_{\text{out}} = u_4 - u_1 = c_v(T_4 - T_1)$$

Then the thermal efficiency of the ideal Diesel cycle under the cold-air- standard assumptions becomes

$$\eta_{th,Diesel} = \frac{w_{net}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}} = 1 - \frac{T_4 - T_1}{k(T_3 - T_2)} = 1 - \frac{T_1(T_4/T_1 - 1)}{kT_2(T_3/T_2 - 1)}$$

The define a new quantity, the **cutoff ratio r_c** , as the ratio of the cylinder volumes after and before the combustion process:

$$r_c = \frac{V_3}{V_2} = \frac{V_3}{V_2}$$

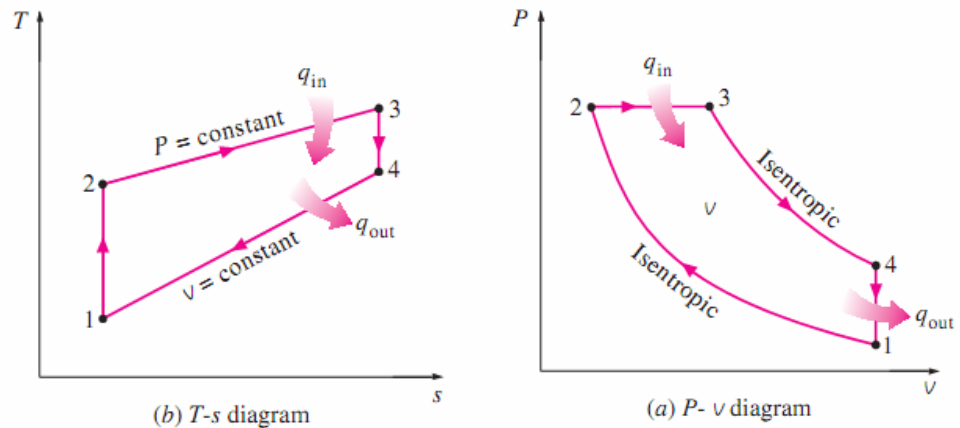
Utilizing this definition and the isentropic ideal-gas relations for processes 1-2 and 3-4, the thermal efficiency relation reduces to

$$\eta_{th,Diesel} = 1 - \frac{1}{r^{k-1}} \left[\frac{r_c^k - 1}{k(r_c - 1)} \right]$$

One would notice that under the cold-air-standard assumptions, the efficiency of a Diesel cycle differs from the efficiency of an Otto cycle by the quantity in the brackets. This quantity is always greater than 1. Therefore,

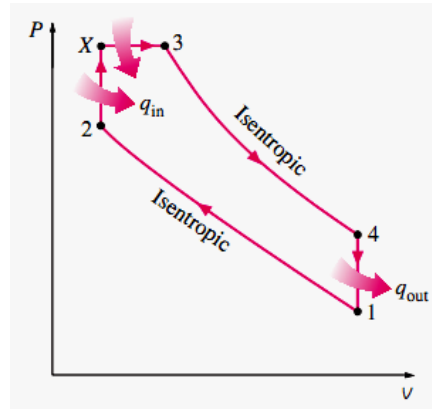
$$\eta_{th,Otto} > \eta_{th,Diesel}$$

FIGURE 14
T-s and P-v diagrams for
the ideal Diesel cycle



Approximating the combustion process in internal combustion engines as a constant-volume or a constant-pressure heat-addition process is overly simplistic and not quite realistic. Probably a better (but slightly more complex) the combustion process in both gasoline and diesel engines as a combination of two heat-transfer processes, one at constant volume and the other at constant pressure. The ideal cycle based on this concept is called the dual cycle, and a P-v diagram for it is given in Fig.15. The relative amounts of heat transferred during each process can be adjusted to approximate the actual cycle more closely. Note that both the Otto and the Diesel cycles can be obtained as special cases of the dual cycle.

FIGURE 15
P-v diagram of an ideal dual cycle



Ex3- An air-standard Diesel cycle has a compression ratio of 16 and a cutoff ratio of 2. At the beginning of the compression process, air is at 95 kPa and 27°C. Accounting for the variation of specific heats with temperature, determine (a) the temperature after the heat-addition process, (b) the thermal efficiency, and (c) the mean effective pressure

Ans.

Properties The gas constant of air is $R = 0.287 \text{ kJ/kg}\cdot\text{K}$.
The properties of air are given in Table A-17.

Analysis (a) Process 1-2: isentropic compression.

$$T_1 = 300\text{K} \longrightarrow \begin{matrix} u_1 = 214.07\text{kJ/kg} \\ v_{r1} = 621.2 \end{matrix}$$

$$v_{r2} = \frac{v_2}{v_1} v_{r1} = \frac{1}{r} v_{r1} = \frac{1}{16} (621.2) = 38.825 \longrightarrow \begin{matrix} T_2 = 862.4 \text{ K} \\ h_2 = 890.9 \text{ kJ/kg} \end{matrix}$$

Process 2-3: $P = \text{constant}$ heat addition.

$$\frac{P_3 v_3}{T_3} = \frac{P_2 v_2}{T_2} \longrightarrow T_3 = \frac{v_3}{v_2} T_2 = 2T_2 = (2)(862.4 \text{ K}) = 1724.8 \text{ K} \longrightarrow \begin{matrix} h_3 = 1910.6 \text{ kJ/kg} \\ v_{r3} = 4.546 \end{matrix}$$

(b) $q_{\text{in}} = h_3 - h_2 = 1910.6 - 890.9 = 1019.7 \text{ kJ/kg}$

Process 3-4: isentropic expansion.

$$v_{r4} = \frac{v_4}{v_3} v_{r3} = \frac{v_4}{2v_2} v_{r3} = \frac{r}{2} v_{r3} = \frac{16}{2} (4.546) = 36.37 \longrightarrow u_4 = 659.7 \text{ kJ/kg}$$

Process 4-1: $v = \text{constant}$ heat rejection.

$$q_{\text{out}} = u_4 - u_1 = 659.7 - 214.07 = 445.63 \text{ kJ/kg}$$

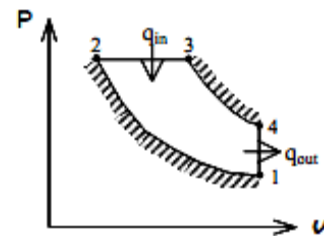
$$\eta_{\text{th}} = 1 - \frac{q_{\text{out}}}{q_{\text{in}}} = 1 - \frac{445.63 \text{ kJ/kg}}{1019.7 \text{ kJ/kg}} = 56.3\%$$

(c) $w_{\text{net,out}} = q_{\text{in}} - q_{\text{out}} = 1019.7 - 445.63 = 574.07 \text{ kJ/kg}$

$$v_1 = \frac{RT_1}{P_1} = \frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(300 \text{ K})}{95 \text{ kPa}} = 0.906 \text{ m}^3/\text{kg} = v_{\text{max}}$$

$$v_{\text{min}} = v_2 = \frac{v_{\text{max}}}{r}$$

$$\text{MEP} = \frac{w_{\text{net,out}}}{v_1 - v_2} = \frac{w_{\text{net,out}}}{v_1 (1 - 1/r)} = \frac{574.07 \text{ kJ/kg}}{(0.906 \text{ m}^3/\text{kg})(1 - 1/16)} \left(\frac{\text{kPa} \cdot \text{m}^3}{\text{kJ}} \right) = 675.9 \text{ kPa}$$

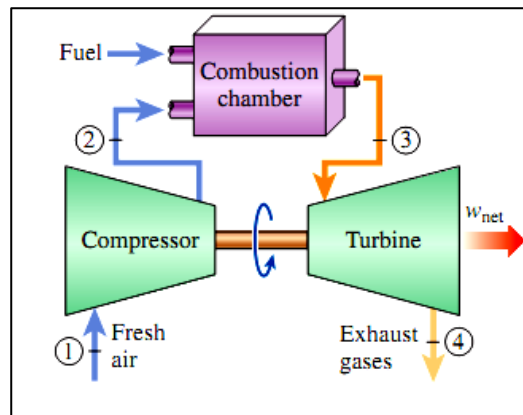


7- BRAYTON CYCLE: THE IDEAL CYCLE FOR GAS-TURBINE ENGINES

The Brayton cycle use in the reciprocating oil-burning engine .Today, it is used for gas turbines only where both the compression and expansion processes take place in rotating machinery. Gas turbines usually operate on an open cycle, as shown in Fig.16. Fresh air at ambient conditions is drawn into the compressor, where its temperature and pressure are raised. The high-pressure air proceeds into the combustion chamber, where the fuel is burned at constant pressure. The resulting high-temperature gases then enter the turbine, where they expand to the atmospheric pressure while producing power. The exhaust gases leaving the turbine are thrown out (not recirculated), causing the cycle to be classified as an open cycle.

FIGURE 16

An open-cycle gas-turbine engine.

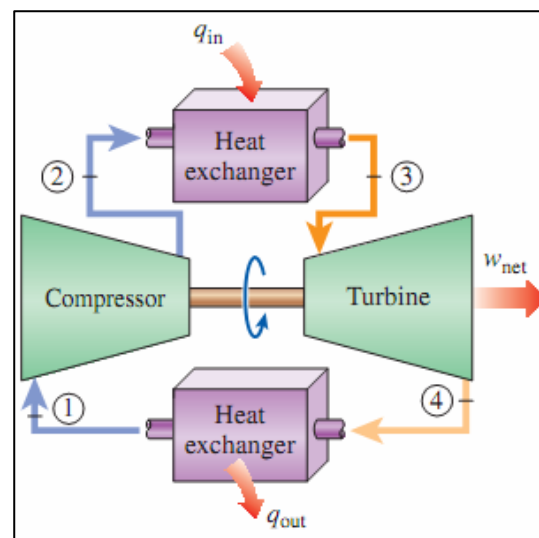


The open gas-turbine cycle described above can be modeled as a closed cycle, as shown in Fig. 17, by utilizing the air-standard assumptions. Here the compression and expansion processes remain the same, but the combustion process is replaced by a constant-pressure heat-addition process from an external source, and the exhaust process is replaced by a constant-pressure heat-rejection process to the ambient air. The ideal cycle that the working fluid undergoes in this closed loop is the **Brayton** cycle, which is made up of four internally reversible processes:-

- 1-2 Isentropic compression (in a compressor)
- 2-3 Constant-pressure heat addition
- 3-4 Isentropic expansion (in a turbine)
- 4-1 Constant-pressure heat rejection

FIGURE 17

A closed-cycle gas-turbine engine.



The T-s and P-v diagrams of an ideal Brayton cycle are shown in Fig. 18. Notice that all four processes of the Brayton cycle are executed in steady-flow devices; thus, they should be analyzed as steady-flow processes. When the changes in kinetic and potential energies are neglected, the energy balance for a steady-flow process can be expressed, on a unit-mass basis, as

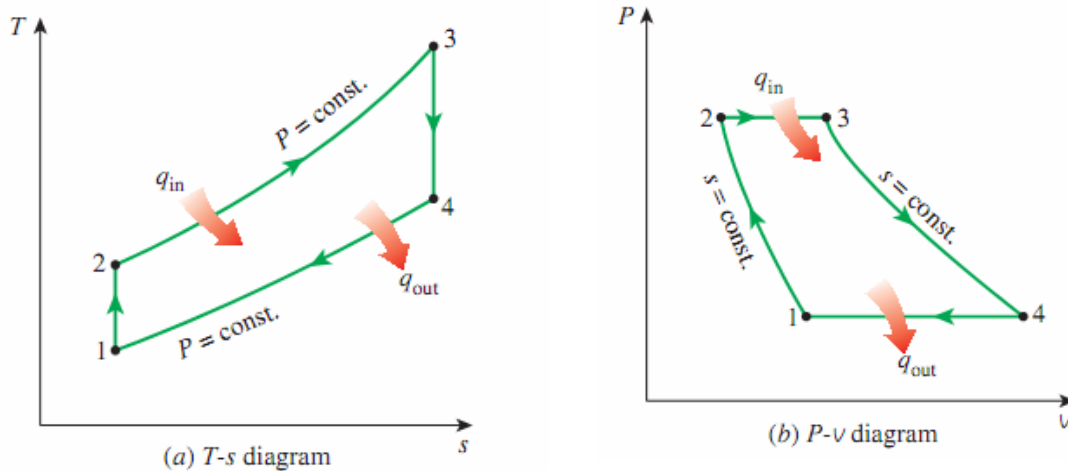


FIGURE 18 T-s and P-v diagrams for the ideal Brayton cycle.

$$(q_{in} - q_{out}) + (w_{in} - w_{out}) = h_{exit} - h_{inlet}$$

Therefore, heat transfers to and from the working fluid are

$$q_{in} = h_3 - h_2 = c_p(T_3 - T_2)$$

and

$$q_{out} = h_4 - h_1 = c_p(T_4 - T_1)$$

Then the thermal efficiency of the ideal Brayton cycle under the cold-air-standard assumptions becomes

$$\eta_{th, Brayton} = \frac{w_{net}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}} = 1 - \frac{c_p(T_4 - T_1)}{c_p(T_3 - T_2)} = 1 - \frac{T_1(T_4/T_1 - 1)}{T_2(T_3/T_2 - 1)}$$

Processes 1-2 and 3-4 are isentropic, and $P_2 = P_3$ and $P_4 = P_1$. Thus,

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} = \left(\frac{P_3}{P_4}\right)^{(k-1)/k} = \frac{T_3}{T_4}$$

Substituting these equations into the thermal efficiency relation and simplifying give

$$\eta_{th, Brayton} = 1 - \frac{1}{r_p^{(k-1)/k}}$$

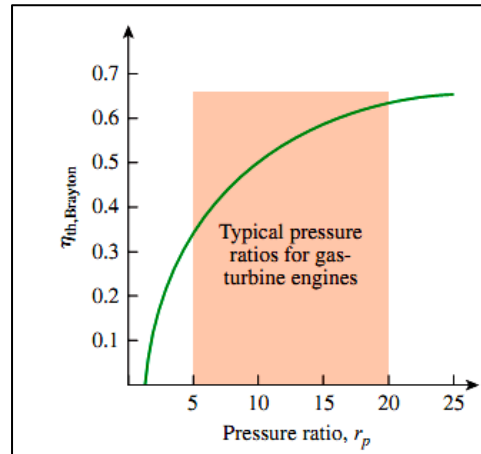
where

$$r_p = \frac{P_2}{P_1}$$

is the pressure ratio and k is the specific heat ratio. The thermal efficiency of an ideal Brayton cycle depends on the pressure ratio of the gas turbine and the specific heat ratio of the working fluid. The thermal efficiency increases with both of these parameters, which is also the case for actual gas turbines. A plot of thermal efficiency versus the pressure ratio is given in Fig.19 for $k = 1.4$, which is the specific-heat-ratio value of air at room temperature. The highest temperature in the cycle occurs at the end of the combustion process (state 3), and it is limited by the maximum temperature that the turbine blades can withstand. This also limits the pressure ratios that can be used in the cycle.

FIGURE 19

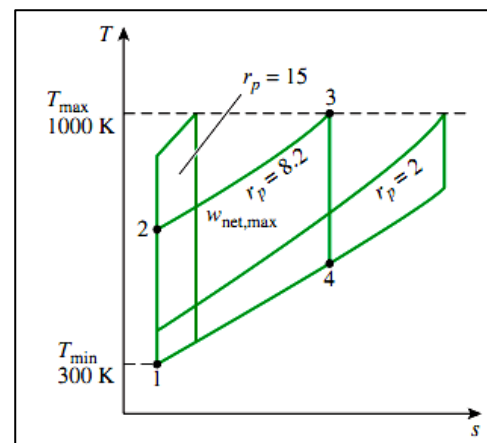
Thermal efficiency of the ideal Brayton cycle as a function of the pressure ratio.



For a fixed turbine inlet temperature T_3 , the net work output per cycle increases with the pressure ratio, reaches a maximum, and then starts to decrease, as shown in Fig.20. Therefore, there should be a compromise between the pressure ratio (thus the thermal efficiency) and the net work output. With less work output per cycle, a larger mass flow rate (thus a larger system) is needed to maintain the same power output, which may not be economical. In most common designs, the pressure ratio of gas turbines ranges from about 11 to 16.

FIGURE 20

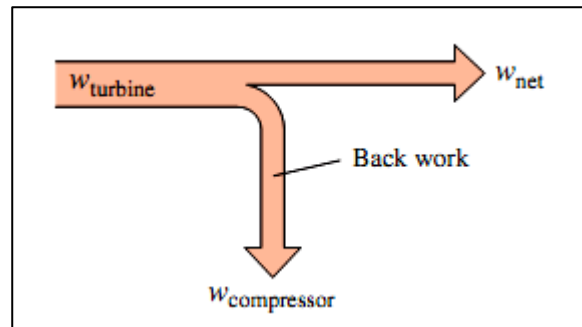
For fixed values of T_{\min} and T_{\max} , the net work of the Brayton cycle first increases with the pressure ratio, then reaches a maximum at $r_p = (T_{\max}/T_{\min})^{k/[2(k-1)]}$, and finally decreases.



In gas-turbine power plants, the ratio of the compressor work to the turbine work, called the back work ratio, is very high (Fig.21). Usually more than one-half of the turbine work output is used to drive the compressor. The situation is even worse when the isentropic efficiencies of the compressor and the turbine are low. This is quite in contrast to steam power plants, where the **back work ratio** is only a few percent.

FIGURE 21

The fraction of the turbine work used to drive the compressor is called the back work ratio.



A gas turbine manufactured by General Electric in the early 1990s had a pressure ratio of 13.5 and generated 135.7 MW of net power at a thermal efficiency of 33 percent in simple-cycle operation. A more recent gas turbine manufactured by General Electric uses a turbine inlet temperature of 1425 C (2600 F) and produces up to 282 MW while achieving a thermal efficiency of 39.5 percent in the simple-cycle mode. A 1.3-ton small-scale gas turbine labeled OP-16, built by the Dutch firm Opra Optimal Radial Turbine, can run on gas or liquid fuel and can replace a 16-ton diesel engine. It has a pressure ratio of 6.5 and produces up to 2 MW of power. Its efficiency is 26 percent in the simple-cycle operation, which rises to 37 percent when equipped with a regenerator.

Ex.1 A gas-turbine power plant operating on an ideal Brayton cycle has a pressure ratio of 8. The gas temperature is 300 K at the compressor inlet and 1300 K at the turbine inlet. Utilizing the air-standard assumptions, determine (a) the gas temperature at the exits of the compressor and the turbine, (b) the back work ratio, and (c) the thermal efficiency.

(a) The air temperatures at the compressor and turbine exits are determined from isentropic relations:

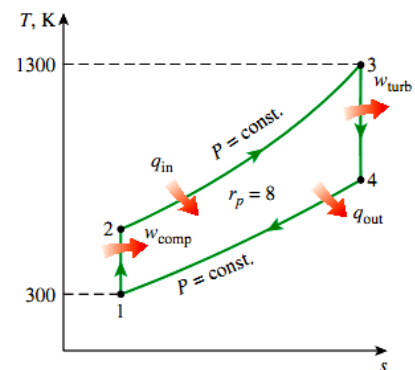
Process 1–2 (isentropic compression of an ideal gas):

$$T_1 = 300 \text{ K} \rightarrow h_1 = 300.19 \text{ kJ/kg}$$

$$P_{r1} = 1.386$$

$$P_{r2} = \frac{P_2}{P_1} P_{r1} = (8)(1.386) = 11.09 \rightarrow T_2 = 540 \text{ K} \quad (\text{at compressor exit})$$

$$h_2 = 544.35 \text{ kJ/kg}$$



Process 3–4 (isentropic expansion of an ideal gas):

$$T_3 = 1300 \text{ K} \rightarrow h_3 = 1395.97 \text{ kJ/kg}$$

$$P_{r3} = 330.9$$

$$P_{r4} = \frac{P_4}{P_3} P_{r3} = \left(\frac{1}{8}\right)(330.9) = 41.36 \rightarrow T_4 = 770 \text{ K} \quad (\text{at turbine exit})$$

$$h_4 = 789.37 \text{ kJ/kg}$$

(b) To find the back work ratio, we need to find the work input to the compressor and the work output of the turbine:

$$w_{\text{comp, in}} = h_2 - h_1 = 544.35 - 300.19 = 244.16 \text{ kJ/kg}$$

$$w_{\text{turb, out}} = h_3 - h_4 = 1395.97 - 789.37 = 606.60 \text{ kJ/kg}$$

Thus,

$$r_{\text{bw}} = \frac{w_{\text{comp, in}}}{w_{\text{turb, out}}} = \frac{244.16 \text{ kJ/kg}}{606.60 \text{ kJ/kg}} = 0.403$$

That is, 40.3 percent of the turbine work output is used just to drive the compressor.

(c) The thermal efficiency of the cycle is the ratio of the net power output to the total heat input:

$$q_{\text{in}} = h_3 - h_2 = 1395.97 - 544.35 = 851.62 \text{ kJ/kg}$$

$$w_{\text{net}} = w_{\text{out}} - w_{\text{in}} = 606.60 - 244.16 = 362.4 \text{ kJ/kg}$$

Thus,

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{362.4 \text{ kJ/kg}}{851.62 \text{ kJ/kg}} = 0.426 \text{ or } 42.6\%$$

The thermal efficiency could also be determined from

$$\eta_{\text{th}} = 1 - \frac{q_{\text{out}}}{q_{\text{in}}}$$

where

$$q_{\text{out}} = h_4 - h_1 = 789.37 - 300.19 = 489.2 \text{ kJ/kg}$$

$$\eta_{\text{th, Brayton}} = 1 - \frac{1}{r_p^{(k-1)/k}} = 1 - \frac{1}{8^{(1.4-1)/1.4}} = 0.448 \text{ or } 44.8\%$$

8-THE BRAYTON CYCLE WITH REGENERATION

In gas-turbine engines, the temperature of the exhaust gas leaving the turbine is often considerably higher than the temperature of the air leaving the compressor. Therefore, the high-pressure air leaving the compressor can be heated by transferring heat to it from the hot exhaust gases in a counter-flow heat exchanger, which is also known as a regenerator or a recuperator. A sketch of the gas-turbine engine utilizing a regenerator and the T-s diagram of the new cycle are shown in Figs. 22 and 23, respectively.

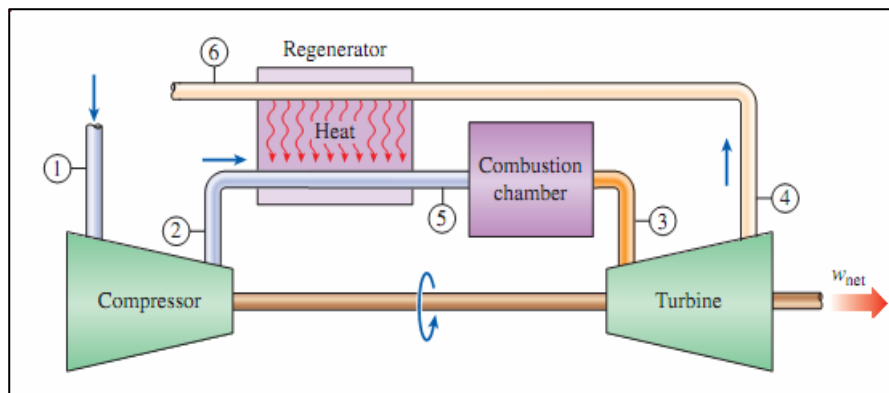


FIGURE 22 A gas-turbine engine with regenerator

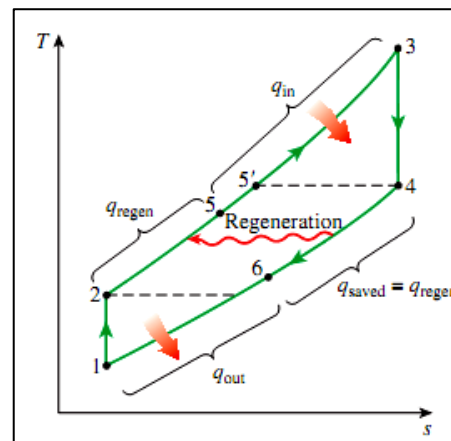


FIGURE 23

T-s diagram of a Brayton cycle with regeneration.

The highest temperature occurring within the regenerator is T_4 , the temperature of the exhaust gases leaving the turbine and entering the regenerator. Under no conditions can the air be preheated in the regenerator to a temperature above this value. Air normally leaves the regenerator at a lower temperature, T_5 . In the limiting (ideal) case, the air exits the regenerator at the inlet temperature of the exhaust gases T_4 . Assuming the regenerator to be well insulated and any changes in kinetic and potential energies to be negligible, the actual and maximum heat transfers from the exhaust gases to the air can be expressed as

$$q_{\text{regen,act}} = h_5 - h_2$$

and

$$q_{\text{regen,max}} = h_{5'} - h_2 = h_4 - h_2$$

The extent to which a regenerator approaches an ideal regenerator is called the **effectiveness** ϵ and is defined as

$$\epsilon = \frac{q_{\text{regen,act}}}{q_{\text{regen,max}}} = \frac{h_5 - h_2}{h_4 - h_2}$$

When the cold-air-standard assumptions are utilized, it reduces to

$$\epsilon \cong \frac{T_5 - T_2}{T_4 - T_2}$$

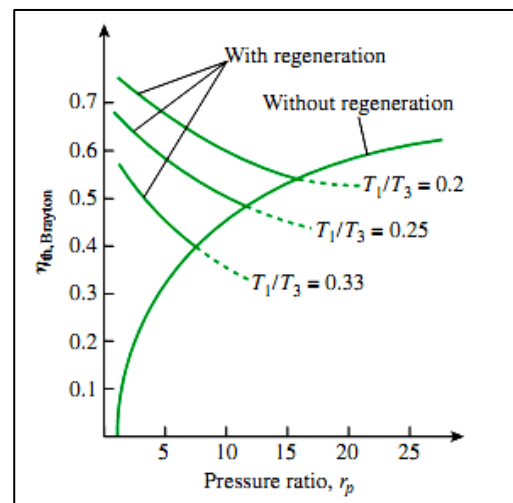
A regenerator with a higher effectiveness obviously saves a greater amount of fuel since it preheats the air to a higher temperature prior to combustion. However, achieving a higher effectiveness requires the use of a larger regenerator, which carries a higher price tag and causes a larger pressure drop. Therefore, the use of a regenerator with a very high effectiveness cannot be justified economically unless the savings from the fuel costs exceed the additional expenses involved. The effectiveness of most regenerators used in practice is below 0.85.

Under the cold-air-standard assumptions, the thermal efficiency of an ideal Brayton cycle with regeneration is

$$\eta_{\text{th,regen}} = 1 - \left(\frac{T_1}{T_3} \right) (r_p)^{(k-1)/k}$$

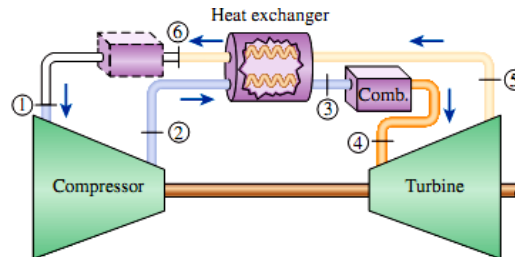
Therefore, the thermal efficiency of an ideal Brayton cycle with regeneration depends on the ratio of the minimum to maximum temperatures as well as the pressure ratio. The thermal efficiency is plotted in Fig. 24 for various pressure ratios and minimum-to-maximum temperature ratios. This figure shows that regeneration is most effective at lower pressure ratios and low minimum-to-maximum temperature ratios.

FIGURE 24
Thermal efficiency of the ideal
Brayton cycle with and without
regeneration



Ex.2 A gas turbine for an automobile is designed with a regenerator. Air enters the compressor of this engine at 100 kPa and 30°C. The compressor pressure ratio is 10; the maximum cycle temperature is 800°C; and the cold air stream leaves the regenerator 10°C cooler than the hot air stream at the inlet of the regenerator. Assuming both the compressor and the turbine to be isentropic, determine the rates of heat addition and rejection for this cycle when it produces 115 kW. Use constant specific heats at room temperature.

Ans.



$$T_2 = T_1 r_p^{(k-1)/k} = (303 \text{ K})(10)^{0.4/1.4} = 585.0 \text{ K}$$

$$T_5 = T_4 \left(\frac{1}{r_p} \right)^{(k-1)/k} = (1073 \text{ K}) \left(\frac{1}{10} \right)^{0.4/1.4} = 555.8 \text{ K}$$

When the first law is applied to the heat exchanger, the result is

$$T_3 - T_2 = T_5 - T_6$$

while the regenerator temperature specification gives

$$T_3 = T_5 - 10 = 555.8 - 10 = 545.8 \text{ K}$$

The simultaneous solution of these two results gives

$$T_6 = T_5 - (T_3 - T_2) = 555.8 - (545.8 - 585.0) = 595.0 \text{ K}$$

Application of the first law to the turbine and compressor gives

$$\begin{aligned} w_{\text{net}} &= c_p (T_4 - T_5) - c_p (T_2 - T_1) \\ &= (1.005 \text{ kJ/kg} \cdot \text{K})(1073 - 555.8) \text{ K} - (1.005 \text{ kJ/kg} \cdot \text{K})(585.0 - 303) \text{ K} \\ &= 236.4 \text{ kJ/kg} \end{aligned}$$

Then,

$$\dot{m} = \frac{\dot{W}_{\text{net}}}{w_{\text{net}}} = \frac{115 \text{ kW}}{236.4 \text{ kJ/kg}} = 0.4864 \text{ kg/s}$$

Applying the first law to the combustion chamber produces

$$\dot{Q}_{\text{in}} = \dot{m} c_p (T_4 - T_3) = (0.4864 \text{ kg/s})(1.005 \text{ kJ/kg} \cdot \text{K})(1073 - 545.8) \text{ K} = \mathbf{258 \text{ kW}}$$

Similarly,

$$\dot{Q}_{\text{out}} = \dot{m} c_p (T_6 - T_1) = (0.4864 \text{ kg/s})(1.005 \text{ kJ/kg} \cdot \text{K})(595.0 - 303) \text{ K} = \mathbf{143 \text{ kW}}$$

