

CHAPTER FOUR

First Law of Thermodynamics And Energy

4.1 The first law of thermodynamics

- The first law of thermodynamics: The total change in energy of a system is the sum of the heat added to it and the work done on it

$$\Delta E = Q - W$$

(conservation of energy)

- **Remember:**
 - Q_{in} is positive
 - Q_{out} is negative
 - W done *by* the system is positive
 - W done *on* the system is negative

Cont..

- While Q and W depend on the path,
 $\Delta E = Q - W$ does not.
- The change in energy of a system during any thermodynamic process depends only on the initial and final states, not on the path leading from one to the other.
- i.e. E is an *intrinsic property* of the system.

Cont..

- Again, let Δe be the change in energy of the system:

$$\Delta e = q - w$$

- In differential form this becomes

$$de = \delta q - \delta w$$

where: δq is the differential increment of heat added to the system, δw is the differential element of work done on the system, and de the differential increase in energy of the system. This is a statement of the First Law of Thermodynamics.

4.2 The First Law of Thermodynamics for A Control Mass

4.2.1 The First Law of Thermodynamics for a Control Mass Undergoing a Cycle

- The first law of thermodynamics states that during any cycle a system (control mass) undergoes, the cyclic integral of the heat is proportional to the cyclic integral of the work.

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

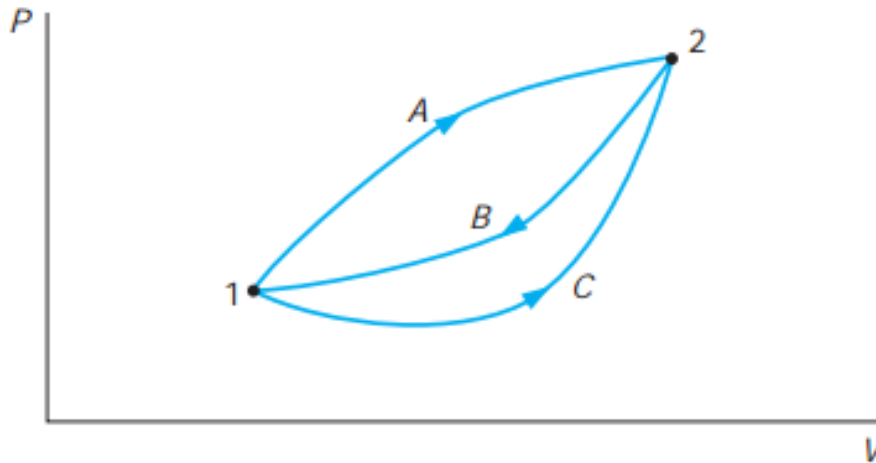
- The symbol $\oint \delta Q$, which is called the cyclic integral of the heat transfer, represents the net heat transfer during the cycle, and, $\oint \delta W$ the cyclic integral of the work, represents the net work during the cycle.
- So the above equation states the first law of thermodynamics for a control mass during a cycle.

4.2.2 The First Law of Thermodynamics For A Change In State of A Control Mass

- We now consider the first law of thermodynamics for a control mass that undergoes a change of state.
- Consider a system that 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 Figure below on a p–v diagram. From the first law of thermodynamics we have

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

Cont..



- 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

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

Cont...

- 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,

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

Cont..

- 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 is given by

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

Cont...

- Because E is a property, its derivative is written dE.
- When dE is integrated from an initial state1 to a final state2, we have

$$E_2 - E_1 = Q_{1-2} - W_{1-2}$$

where: E1 and E2 are the initial and final values of the energy E of the control mass, Q_{1-2} is the heat transferred to the control mass during the process from state1 to state2, and W_{1-2} is the work done by the control mass during the process.

Cont..

- For a closed system undergoing a **cycle**, the initial and final states are identical, and thus

$$\Delta E_{system} = E_1 - E_2 = 0, E_1 = E_2$$

- Then the energy balance for a cycle simplifies to

$$E_{in} - E_{out} = 0 \text{ or } E_{in} = E_{out}$$

- Noting that a closed system does not involve any mass flow across its boundaries, the energy balance for a cycle can be expressed in terms of heat and work interactions as

$$W_{net,out} = Q_{net,in} \quad \text{or} \quad \dot{W}_{net,out} = \dot{Q}_{net,in} \quad (\text{for a cycle})$$

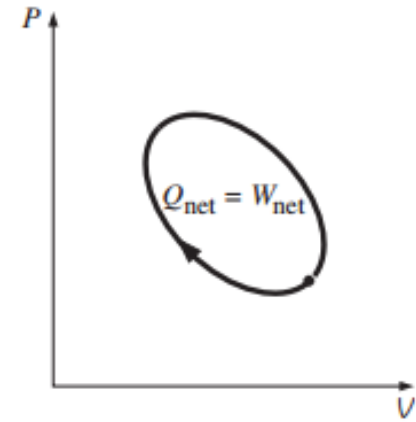


Fig:1 For a cycle $\Delta E = 0$, thus $Q = W$

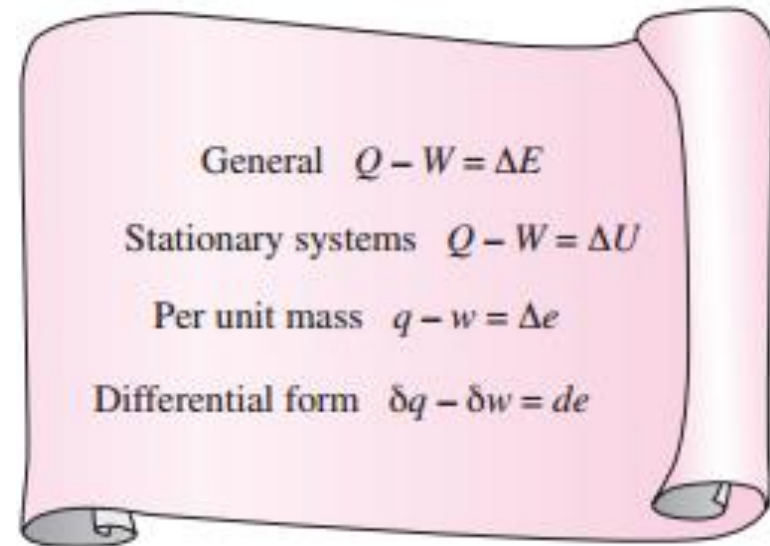


Fig: 2 Various forms of the first-law relation for closed systems

Cont..

- The physical significance of the property E is that it represents all the energy of the system in the given state.
- This energy might be present in a variety of forms, such as
 - ✓ the kinetic or potential energy of the system as a whole with respect to the chosen coordinate frame
 - ✓ energy associated with the motion and position of the molecules
 - ✓ energy associated with the structure of the atom
 - ✓ chemical energy present in a storage battery
 - ✓ energy present in a charged capacitor, or any of a number of other forms.

Cont...

- 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

$$E = U + KE + PE$$

Cont..

- The **kinetic** and **potential energy** of the control mass are associated with the coordinate frame that we select and can be specified by the macroscopic parameters of mass, velocity, and elevation.
- The internal energy U includes all other forms of energy of the control mass and is associated with the thermodynamic state of the system.
- Since the terms comprising E are point functions, we can write

$$dE = dU + d(\text{KE}) + d(\text{PE})$$

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

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

Cont...

- In words, this equation states that as a control mass undergoes a change of state, energy may cross the boundary as either heat or work, and each may be positive or negative.
- The net change in the energy of the system will be exactly equal to the net energy that crosses the boundary of the system.
- The energy of the system may change in any of three ways by a change in internal energy, in kinetic energy, or in potential energy.

Cont..

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

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

But

$$\delta W = -F dx = -d\text{KE}$$

Cont...

$$F = ma = m \frac{d\mathbf{V}}{dt} = m \frac{dx}{dt} \frac{d\mathbf{V}}{dx} = m\mathbf{V} \frac{d\mathbf{V}}{dx}$$

- Then

$$d\text{KE} = F dx = m\mathbf{V} d\mathbf{V}$$

- Integrating, we obtain

$$\int_{\text{KE}=0}^{\text{KE}} d\text{KE} = \int_{\mathbf{V}=0}^{\mathbf{V}} m\mathbf{V} d\mathbf{V}$$

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

Cont..

- 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 . From the first law we have

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

$$F = ma = mg$$

Then

$$dPE = F dZ = mg dZ$$

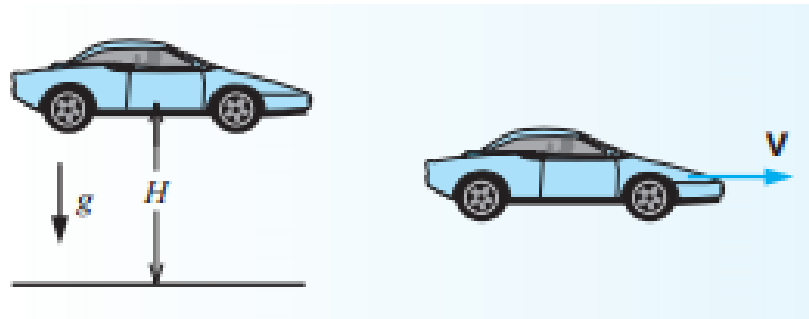
Integrating gives

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

Cont..

Example 1

- A car of mass 1100 kg drives with a velocity such that it has a kinetic energy of 400 kJ (see in the Figure). 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?



Cont...

Example 2

Consider a stone having a mass of 10 kg and a bucket containing 100 kg of liquid water. Initially the stone is 10.2 m above the water, and the stone and the water are at the same temperature, state 1. The stone then falls into the water. Determine ΔU , $\Delta K.E$, $\Delta P.E$, Q , and W for the following changes of state.

- a. The stone is about to enter the water, state 2.
- b. The stone has just come to rest in the bucket, state 3.
- c. Heat has been transferred to the surroundings in such an amount that the stone and water are at the same temperature, T_1 , state 4.

4.3 Internal Energy-A Thermodynamic Property

$$U = \sum (KE) + \sum (PE)$$

Random chaotic motion interaction between atoms & molecules

- The kinetic and potential energies associated with the random motion of molecules constitute the *internal energy* U .
- Value of U not important, ΔU during a thermal process is what matters:

$$\Delta U = U_2 - U_1 = U_{final} - U_{initial}$$

Cont...

- Internal energy is an extensive property because it depends on the mass of the system.
- Kinetic and potential energies are also extensive properties.
- tables of thermodynamic properties such as the saturated water tables, the value of internal energy can be tabulated along with other thermodynamic properties.
- the internal energy for saturated states, which include the internal energy of saturated liquid u_f , the internal energy of saturated vapor u_g , and the difference between the internal energy of saturated liquid and saturated vapor u_{fg} .

Cont..

- 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

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

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

Cont...

Example 3

- A vessel having a volume of 5 m³ contains 0.05 m³ of saturated liquid water and 4.95 m³ of saturated water vapor at 0.1 MPa. Heat is transferred until the vessel is filled with saturated vapor. Determine the heat transfer for this process

4.4 THE THERMODYNAMIC PROPERTY ENTHALPY

- Let us consider a control mass undergoing a quasi-equilibrium constant-pressure process, as shown in Figure.

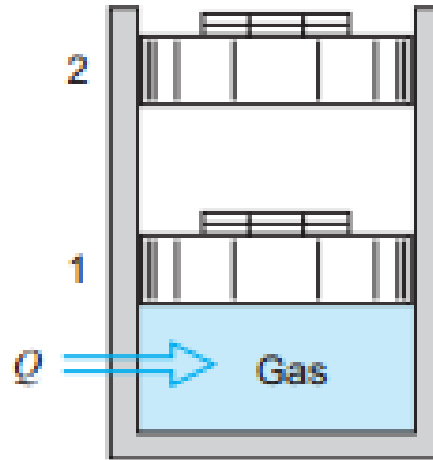


Figure 5.1: The constant-pressure quasi-equilibrium process

- 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 of thermodynamics we have, in terms of Q ,

Cont...

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

- 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

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

Cont...

- We find that, in this very restricted case, 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 of the state of the system only, therefore their combination must also have these same characteristics.
- So, it is convenient to define a new extensive property, the enthalpy

$$H \equiv U + PV$$

or, per unit mass,

$$h \equiv u + Pv$$

Cont...

- The enthalpy of a substance in a saturation state and with a given quality is found in the same way as the specific volume and internal energy.
- The enthalpy of saturated liquid has the symbol h_f , saturated vapor h_g , and the increase in enthalpy during vaporization h_{fg} .
- For a saturation state, the enthalpy can be calculated by one of the following relations:

$$h = (1 - x)h_f + xh_g$$

$$h = h_f + xh_{fg}$$

- The enthalpy of compressed liquid water may be found from Table A7 compressed liquid table.
- For substances for which compressed-liquid tables are not available, the enthalpy is taken as that of saturated liquid at the same temperature.

$$h_f \approx h$$

Cont...

Example

1. 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.
2. Saturated-vapor R-134a is contained in a piston/cylinder at room temperature, 20°C , at which point the cylinder volume is 10 L . The external force restraining the piston is now reduced, allowing the system to expand to 40 L . We will consider two different situations:
 - a. The cylinder is uninsulated. In addition, the external force is reduced very slowly as the process takes place. If the work done during the process is 8.0 kJ , how much heat is transferred?
 - b. The cylinder is insulated. Also, the external force is reduced rapidly, causing the process to occur rapidly, such that the final pressure inside the cylinder is 150 kPa . What are the heat transfer and work for this process?

4.5 The Constant-volume And Constant-pressure Specific Heats

- In this section we will 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.
- to examine the relation between the specific heat and other thermodynamic variables, we reminder first that the change in energy of the system with the following restriction will be.
 - Neglecting changes in kinetic and potential energies
 - assuming a simple compressible substance
 - a quasi-equilibrium process with constant pressure
 - the work done during the process is that associated with the boundary movement.

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

Cont...

- 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, and the corresponding specific heat (at constant pressure) is

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

- Note that in each of these special cases, the resulting expression contains only thermodynamic properties, from which we conclude that the constant-volume and constant-pressure specific heats must themselves be thermodynamic properties.

Cont..

Solids and Liquids

- As a special case, consider either a solid or a liquid. Since both of these phases are nearly incompressible, Also, for both of these phases, the specific volume is very small, such that in many cases.

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

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

- 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 in Eq.2 is constant (unless the process occurs at low temperature or over a wide range of temperatures). Equation 2 can then be integrated to

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

- Specific heats for various solids and liquids are listed in Tables A3.
- In other processes for which it is not possible to assume constant specific heat, there may be a known relation for C as a function of temperature. Equation 2 could then also be integrated.

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

- In general, for any substance the internal energy u depends on the two independent properties specifying the state.
- For a low-density gas, however, u depends primarily on T and much less on the second property, P or v .
- For example, consider several values for superheated vapor water from Table A6, From these values, it is evident that u depends strongly on T but not much on P .
- Also, we note that the dependence of u on P is less at low pressure and is much less at high temperature; that is, as the density decreases, so does dependence of u on P (or v).

Cont..

- 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

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

Cont..

- 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 ,

$$dU = mC_{v0} dT$$

Cont..

- 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 earlier

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

- 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

$$dH = mC_{p0} dT$$

Cont..

- The following diagram will demonstrate the strongly relationship between temperature with enthalpy and internal energy

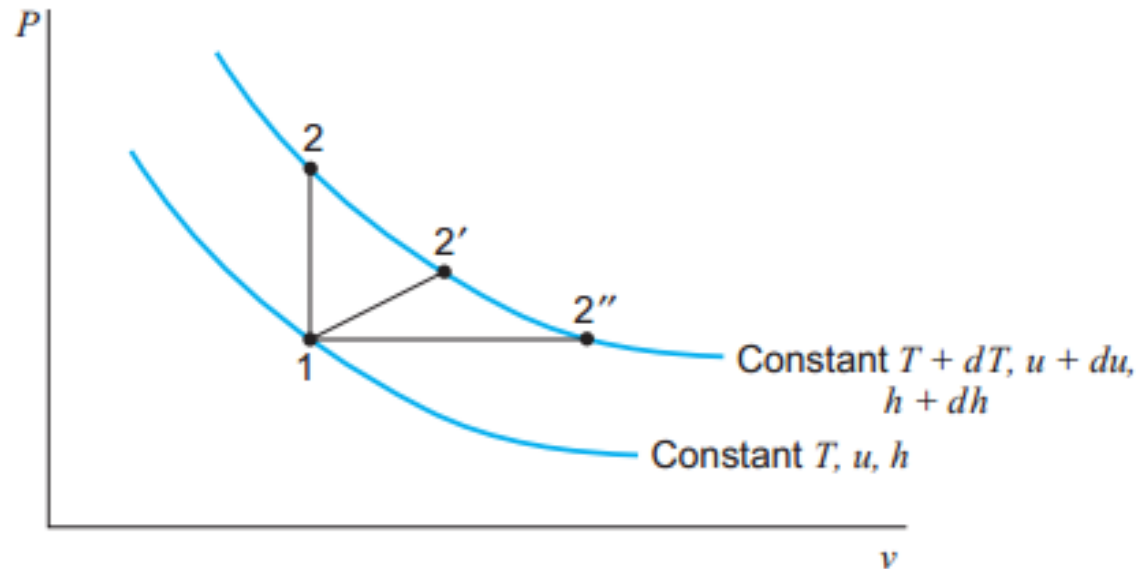


Figure: P - v diagram for an ideal gas

Cont..

- The 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 .
- 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

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

Cont..

- Because all gases approach ideal-gas behavior as the pressure approaches zero, the ideal-gas specific heat for a given substance is often called the *zero-pressure specific heat*, and the zero-pressure, constant-pressure specific heat is given the symbol C_{p0} .
- The zero-pressure, constant-volume specific heat is given the symbol C_{v0} . the Figure below shows C_{p0} as a function of temperature for a number of substances

Cont..

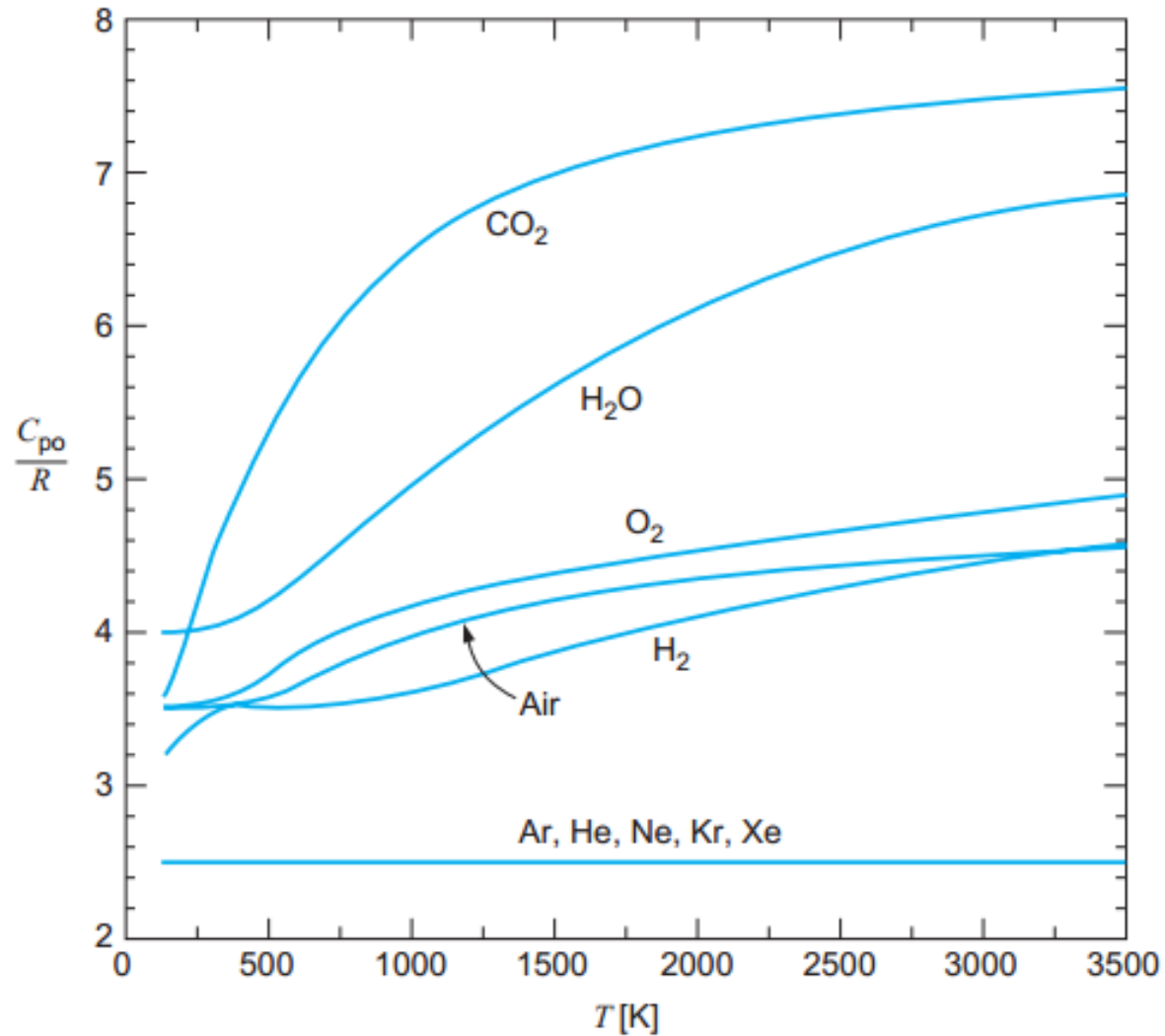


Figure: Heat capacity for some gases as a function of temperature.

Cont..

- 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, we have

$$dh = du + R dT$$

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

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

- On a mole basis this equation is written

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

Cont..

- This tells us that the difference between the constant-pressure and constant-volume specific heats of an ideal gas is always constant, though both are functions of temperature.
- Thus, we need examine only the temperature dependency of one, and the other is given by the above equation.
- 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

$$dh = C_{p0} dT$$

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

Cont..

- The second possibility for the specific heat is to use an analytical equation for C_{p0} as a function of temperature.
- Because the results of specific-heat calculations from statistical thermodynamics do not lend themselves to convenient mathematical forms, these results have been approximated empirically.
- The equations for C_{p0} as a function of temperature are listed in Table as shown for a number of gases.

Cont..

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
<i>n</i> -Octane	C ₈ H ₁₈	−0.053	6.75	−3.67	0.775
Oxygen	O ₂	0.88	−0.0001	0.54	−0.33

Cont..

- 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
- This function can then be tabulated in a single-entry (temperature) table. Then, between any two states 1 and 2 and it is seen that the reference temperature cancels out.

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

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

Cont..

- To summarize the three possibilities, we note that using the ideal-gas tables, Tables A.7 and A.8, gives us the most accurate answer, but that the equations in Table A.6 would give a close empirical approximation.
- Constant specific heat would be less accurate, except for monatomic gases and gases below room temperature.
- It should be remembered that all these results are part of the ideal-gas model, which in many of our problems is not a valid assumption for the behavior of the substance.

Cont..

TABLE A7.1

Ideal-Gas Properties of Air, Standard Entropy at 0.1-MPa (1-Bar) Pressure

T (K)	u (kJ/kg)	h (kJ/kg)	s_T^0 (kJ/kg-K)	T (K)	u (kJ/kg)	h (kJ/kg)	s_T^0 (kJ/kg-K)
200	142.77	200.17	6.46260	1100	845.45	1161.18	8.24449
220	157.07	220.22	6.55812	1150	889.21	1219.30	8.29616
240	171.38	240.27	6.64535	1200	933.37	1277.81	8.34596
260	185.70	260.32	6.72562	1250	977.89	1336.68	8.39402
280	200.02	280.39	6.79998	1300	1022.75	1395.89	8.44046
290	207.19	290.43	6.83521	1350	1067.94	1455.43	8.48539
298.15	213.04	298.62	6.86305	1400	1113.43	1515.27	8.52891
300	214.36	300.47	6.86926	1450	1159.20	1575.40	8.57111
320	228.73	320.58	6.93413	1500	1205.25	1635.80	8.61208
340	243.11	340.70	6.99515	1550	1251.55	1696.45	8.65185
360	257.53	360.86	7.05276	1600	1298.08	1757.33	8.69051
380	271.99	381.06	7.10735	1650	1344.83	1818.44	8.72811
400	286.49	401.30	7.15926	1700	1391.80	1879.76	8.76472
420	301.04	421.59	7.20875	1750	1438.97	1941.28	8.80039
440	315.64	441.93	7.25607	1800	1486.33	2002.99	8.83516

Cont..

TABLE A.8

Ideal-Gas Properties of Various Substances, Entropies at 0.1-MPa (1-Bar) Pressure, Mass Basis

T (K)	Nitrogen, Diatomic (N ₂) $R = 0.2968 \text{ kJ/kg}\cdot\text{K}$ $M = 28.013 \text{ kg/kmol}$			Oxygen, Diatomic (O ₂) $R = 0.2598 \text{ kJ/kg}\cdot\text{K}$ $M = 31.999 \text{ kg/kmol}$		
	u (kJ/kg)	h (kJ/kg)	s_T^0 (kJ/kg·K)	u (kJ/kg)	h (kJ/kg)	s_T^0 (kJ/kg·K)
200	148.39	207.75	6.4250	129.84	181.81	6.0466
250	185.50	259.70	6.6568	162.41	227.37	6.2499
300	222.63	311.67	6.8463	195.20	273.15	6.4168
350	259.80	363.68	7.0067	228.37	319.31	6.5590
400	297.09	415.81	7.1459	262.10	366.03	6.6838
450	334.57	468.13	7.2692	296.52	413.45	6.7954
500	372.35	520.75	7.3800	331.72	461.63	6.8969
550	410.52	573.76	7.4811	367.70	510.61	6.9903
600	449.16	627.24	7.5741	404.46	560.36	7.0768
650	488.34	681.26	7.6606	441.97	610.86	7.1577
700	528.09	735.86	7.7415	480.18	662.06	7.2336
750	568.45	791.05	7.8176	519.02	713.90	7.3051
800	609.41	846.85	7.8897	558.46	766.33	7.3728
850	650.98	903.26	7.9581	598.44	819.30	7.4370
900	693.13	960.25	8.0232	638.90	872.75	7.4981

Cont..

Example

1. Calculate the change of enthalpy as 1 kg of oxygen is heated from 300 to 1500 K. Assume ideal-gas behavior.
2. A cylinder fitted with a piston has an initial volume of 0.1 m³ and contains nitrogen at 150 kPa, 25°C. The piston is moved, compressing the nitrogen until the pressure is 1 MPa and the temperature is 150°C. During this compression process heat is transferred from the nitrogen, and the work done on the nitrogen is 20 kJ. Determine the amount of this heat transfer.

4.7 THE FIRST LAW AS A RATE EQUATION

- It is desirable to use 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 or the rate at which the energy of the control mass changes.
- 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:

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

Cont..

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

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

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

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

- Therefore, the rate equation form of the first law is

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

- We could also write this in the form

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

Cont..

Example

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

4.8 CONSERVATION OF MASS

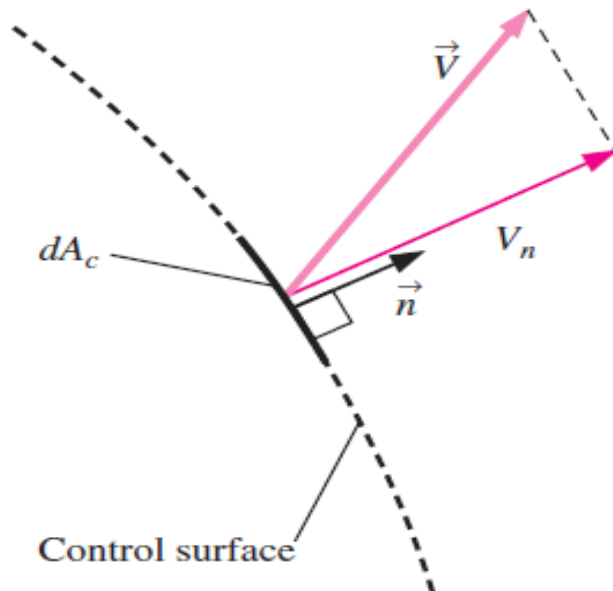
- Conservation of mass is one of the most fundamental principles in nature.
- chemical equations are balanced on the basis of the conservation of mass principle. For example When 16 kg of oxygen reacts with 2 kg of hydrogen, 18 kg of water is formed.
- Mass, like energy, is a conserved property, and it cannot be created or destroyed during a process.

Mass and Volume Flow Rates

- The amount of mass flowing through a cross section per unit time is called the **mass flow rate and is denoted by $\dot{m}$** .
- The dot over a symbol is used to indicate *time rate of change*.

- A fluid usually flows into or out of a control volume through pipes or ducts.
- The differential mass flow rate of fluid flowing across a small area element dA_c on a flow cross section is proportional to dA_c itself, the fluid density ρ , and the component of the flow velocity normal to dA_c , which we denote as v_n , and is expressed as follow

$$\delta \dot{m} = \rho v_n dA_c$$



- The mass flow rate through the entire cross-sectional area of a pipe or duct is obtained by integration:-

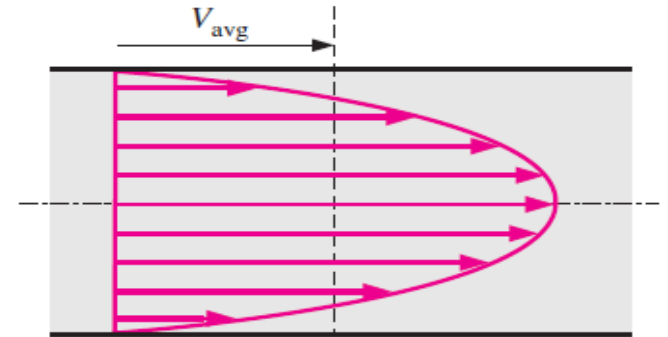
$$\dot{m} = \int_{A_c} \delta \dot{m} = \int_{A_c} \rho V_n dA_c \quad (\text{kg/s})$$

- While the above equation is always valid (in fact it is *exact*), *it is not always practical* for engineering analyses because of the integral. Instead mass flow rate is expressed in terms of average values over a cross section of the pipe.
- In a general compressible flow, both ρ and v_n vary across the pipe. In many practical applications, however, the density is essentially uniform over the pipe cross section and we can take ρ outside the integral of the above Equation.
- Velocity, however, is *never uniform over a cross section of a pipe* because of the fluid sticking to the surface and thus having zero velocity at the wall (the no-slip condition). Rather, the velocity varies from zero at the walls to some maximum value at or near the centerline of the pipe.

- We define the **average velocity** V_{avg} as the average value of across the entire cross section.

Average velocity:

$$V_{avg} = \frac{1}{A_c} \int_{A_c} V_n dA_c$$



- the mass flow rate would be identical to that obtained by integrating the actual velocity profile. Thus for incompressible flow or even for compressible flow where ρ is uniform across A_c , so the above equation becomes:

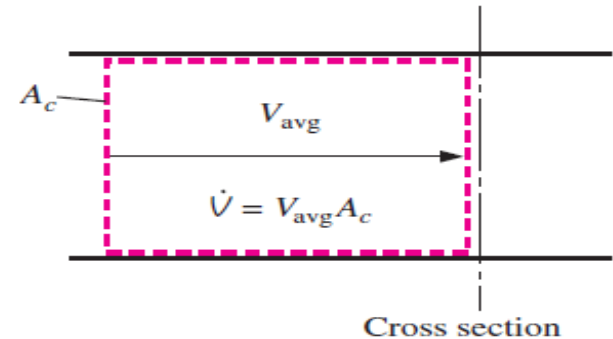
$$\dot{m} = \rho V_{avg} A_c \quad (\text{kg/s})$$

- For simplicity, we drop the subscript on the average velocity. Unless otherwise stated, V denotes the average velocity in the flow direction. Also, A_c denotes the cross-sectional area normal to the flow direction.

$$\dot{m} = \rho V A_c$$

- The volume of the fluid flowing through a cross section per unit time is called the **volume flow rate $\dot{V}$**

$$\dot{V} = \int_{A_c} V_n dA_c = V_{\text{avg}} A_c = V A_c \quad (\text{m}^3/\text{s})$$



- The mass and volume flow rates are related by:

$$\dot{m} = \rho \dot{V} = \frac{\dot{V}}{v}$$

- Where v is the specific volume.
- This relation is analogous to $m = \rho V = \frac{V}{v}$
- which is the relation between the mass and the volume of a fluid in a container.

Cont..

Example

- Air is flowing in a 0.2-m-diameter pipe at a uniform velocity of 0.1 m/s. The temperature is 25°C and the pressure is 150kPa. Determine the mass flow rate.

- The **conservation of mass principle** for a control volume can be expressed as: The net mass transfer to or from a control volume during a time interval Δt is equal to the net change (increase or decrease) in the total mass within the control volume during Δt .

$$\left(\begin{array}{c} \text{Total mass entering} \\ \text{the CV during } \Delta t \end{array} \right) - \left(\begin{array}{c} \text{Total mass leaving} \\ \text{the CV during } \Delta t \end{array} \right) = \left(\begin{array}{c} \text{Net change in mass} \\ \text{within the CV during } \Delta t \end{array} \right)$$

Or

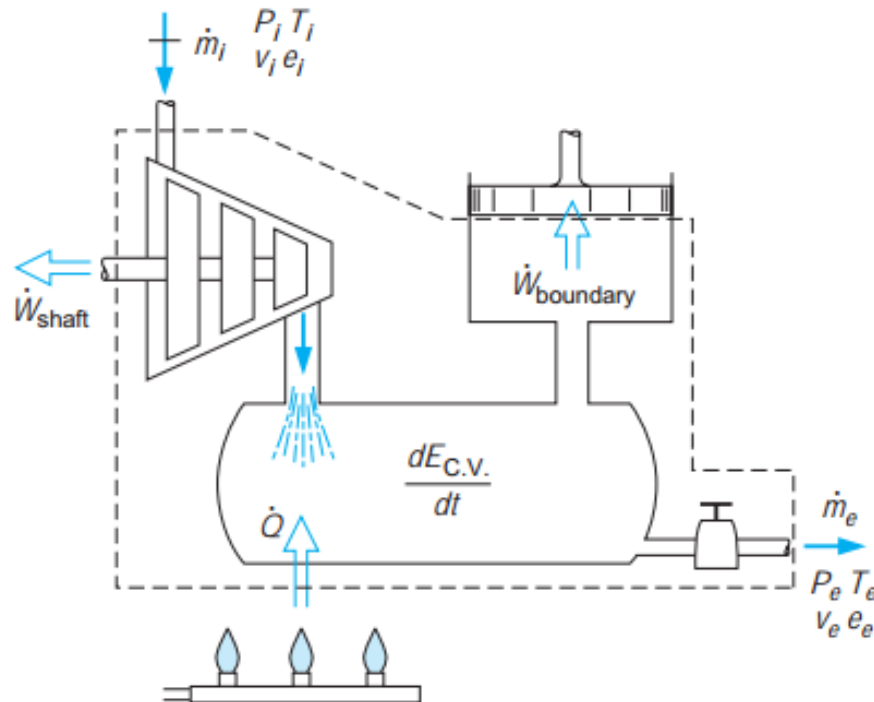
$$m_{in} - m_{out} = \Delta m_{cv}$$

Where: $\Delta m_{cv} = m_{final} - m_{initial}$ is the change in the mass of the control volume during the process.
It can also be expressed in *rate form* as

$$\dot{m}_{in} - \dot{m}_{out} = dm_{CV}/dt \quad (\text{kg/s})$$

4.9 THE FIRST LAW OF THERMODYNAMICS FOR A CONTROL VOLUME

- a control volume is shown in Figure below that involves the rate of heat transfer, rates of work, and mass flows.
- The fundamental physical law states that we cannot create or destroy energy such that any rate of change of energy must be caused by rates of energy into or out of the control volume.



- The fluid flowing across the control surface enters or leaves with an amount of energy per unit mass as

the flow work

$$e = u + \frac{1}{2} \mathbf{V}^2 + gZ$$

$$\dot{W}_{\text{flow}} = F\mathbf{V} = \int P\mathbf{V} dA = P\dot{V} = Pv\dot{m}$$

Where: $\mathbf{V}$ velocity, V volume flow rate and, v specific volume

- For the flow that leaves the control volume, work is being done by the control volume.

$$P_e v_e \dot{m}_e$$

- and for the mass that enters, the surroundings do the rate of work.

$$P_i v_i \dot{m}_i$$

- The flow work per unit mass is then Pv , and the total energy associated with the flow of mass is

$$e + Pv = u + Pv + \frac{1}{2} \mathbf{V}^2 + gZ = h + \frac{1}{2} \mathbf{V}^2 + gZ$$

- Accordingly, the *conservation of energy* principle applied to a control volume states.

$$\left[\begin{array}{c} \text{time rate of change} \\ \text{of the energy} \\ \text{contained within} \\ \text{the control volume at} \\ \text{time } t \end{array} \right] = \left[\begin{array}{c} \text{net rate at which} \\ \text{energy is being} \\ \text{transferred in} \\ \text{by heat transfer} \\ \text{at time } t \end{array} \right] - \left[\begin{array}{c} \text{net rate at which} \\ \text{energy is being} \\ \text{transferred out} \\ \text{by work at} \\ \text{time } t \end{array} \right] + \left[\begin{array}{c} \text{net rate of energy} \\ \text{transfer into the} \\ \text{control volume} \\ \text{accompanying} \\ \text{mass flow} \end{array} \right]$$

- For the one-inlet one-exit control volume the energy rate balance is

$$\frac{dE_{cv}}{dt} = \dot{Q} - \dot{W} + \underbrace{\dot{m}_i \left(u_i + \frac{V_i^2}{2} + gz_i \right)} - \underbrace{\dot{m}_e \left(u_e + \frac{V_e^2}{2} + gz_e \right)}$$

- the work term of the energy rate equation, can be written as

$$\dot{W} = \dot{W}_{cv} + \dot{m}_e(p_e v_e) - \dot{m}_i(p_i v_i)$$

- The term $\dot{W}_{cv}$ accounts for *all other* energy transfers by work across the boundary of the control volume.

- Substitute the second equation to the first one and rearrange.

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_i \left(u_i + p_i v_i + \frac{V_i^2}{2} + gz_i \right) - \dot{m}_e \left(u_e + p_e v_e + \frac{V_e^2}{2} + gz_e \right)$$

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) - \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right)$$

- In practice there may be several locations on the boundary through which mass enters or exits. This can be accounted for by introducing summations as in the mass balance.

Accordingly, the **energy rate balance** is :

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \sum_i \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) - \sum_e \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right)$$

- In principle, the change in the energy of a control volume over a time period can be obtained by integration of the energy rate balance with respect to time.
- Such integrations require information about the time dependences of the work and heat transfer rates, the various mass flow rates, and the states at which mass enters and leaves the control volume.

4.10 THE STEADY-STATE PROCESS

- For a control volume at steady state, the conditions of the mass within the control volume and at the boundary do not vary with time.
- The mass flow rates and the rates of energy transfer by heat and work are also constant with time. There can be no accumulation of mass within the control volume, so $\frac{dm_{cv}}{dt} = 0$ and the mass rate balance takes the form as shown.

$$\begin{array}{ccc} \sum_i \dot{m}_i & = & \sum_e \dot{m}_e \\ \text{(mass rate in)} & & \text{(mass rate out)} \end{array}$$

- Furthermore, at steady state $\frac{dE_{cv}}{dt} = 0$, the rate of energy can be written as

$$\begin{array}{l} 0 = \dot{Q}_{cv} - \dot{W}_{cv} + \sum_i \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) - \sum_e \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right) \\ \dot{Q}_{cv} + \sum_i \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) = \dot{W}_{cv} + \sum_e \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right) \\ \text{(energy rate in)} \qquad \qquad \qquad \text{(energy rate out)} \end{array}$$

- Many of the applications of the steady-state model are such that there is only one flow stream entering and one leaving the control volume. For this type of process, we can write

Continuity equation: $\dot{m}_i = \dot{m}_e = \dot{m}$

First law: $\dot{Q}_{C.V.} + \dot{m} \left(h_i + \frac{\mathbf{v}_i^2}{2} + gZ_i \right) = \dot{m} \left(h_e + \frac{\mathbf{v}_e^2}{2} + gZ_e \right) + \dot{W}_{C.V.}$

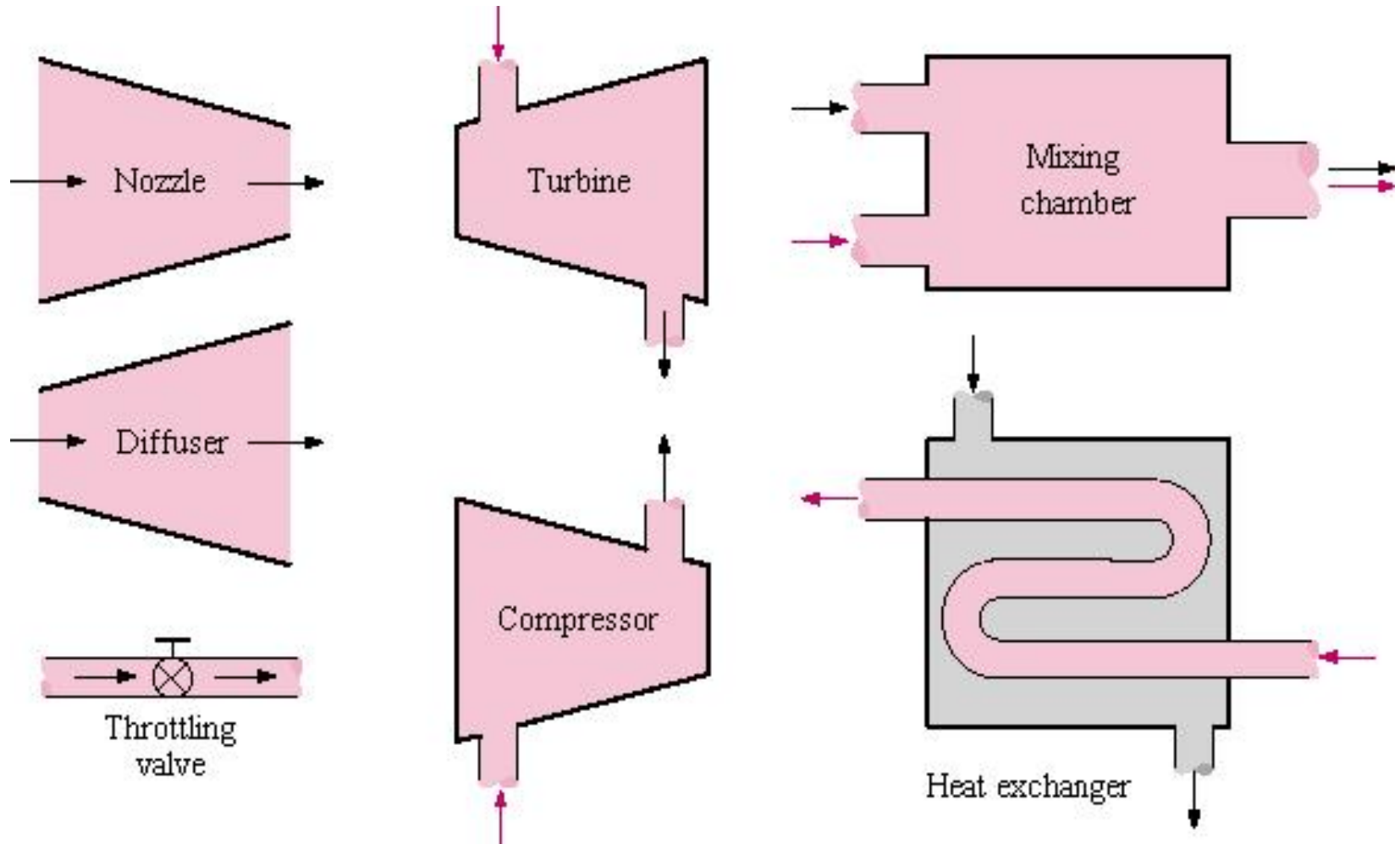
- Rearranging this equation, we have

$$q + h_i + \frac{\mathbf{v}_i^2}{2} + gZ_i = h_e + \frac{\mathbf{v}_e^2}{2} + gZ_e + w$$

where, by definition,

$$q = \frac{\dot{Q}_{C.V.}}{\dot{m}} \quad \text{and} \quad w = \frac{\dot{W}_{C.V.}}{\dot{m}}$$

4.11 EXAMPLES OF STEADY-STATE PROCESSES

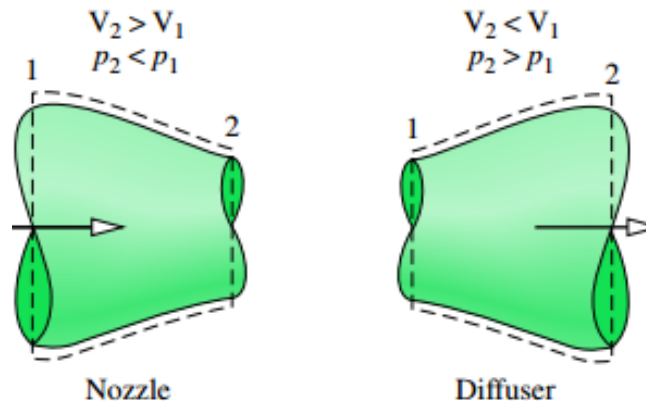


1. NOZZLES AND DIFFUSERS

A **nozzle** is a flow passage of varying cross-sectional area in which the velocity of a gas or liquid increases in the direction of flow.

In a **diffuser**, the gas or liquid decelerates in the direction of flow.

The figure below shows a nozzle in which the cross-sectional area decreases in the direction of flow and a diffuser in which the walls of the flow passage diverge.



- For nozzles and diffusers, the only work is *flow work* at locations where mass enters and exits the control volume, so the term $\dot{W}_{cv}$ drops out of the energy rate equation for these devices.

- The change in potential energy from inlet to exit is negligible under most conditions.
- At steady state the mass and energy rate balances reduce, respectively, to

$$\frac{dm_{cv}}{dt} = \dot{m}_1 - \dot{m}_2$$

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv}^0 + \dot{m}_1 \left(h_1 + \frac{V_1^2}{2} + gz_1 \right) - \dot{m}_2 \left(h_2 + \frac{V_2^2}{2} + gz_2 \right)$$

- where 1 denotes the inlet and 2 the exit. By combining these into a single expression and dropping the potential energy change from inlet to exit

$$0 = \frac{\dot{Q}_{cv}}{\dot{m}} + (h_1 - h_2) + \left(\frac{V_1^2 - V_2^2}{2} \right)$$

- The term representing heat transfer with the surroundings per unit of mass flowing through the nozzle or diffuser is often small enough relative to the enthalpy and kinetic energy changes that it can be dropped.

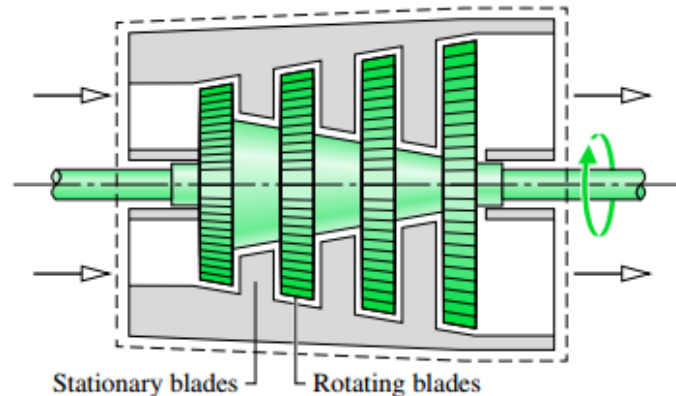
Example

Steam enters a converging–diverging nozzle operating at steady state with $p_1 = 40$ bar, $T_1 = 400^\circ\text{C}$, and a velocity of 10 m/s. The steam flows through the nozzle with negligible heat transfer and no significant change in potential energy. At the exit, $p_2 = 15$ bar, and the velocity is 665 m/s. The mass flow rate is 2 kg/s. Determine the exit area of the nozzle, in m^2 .

2. TURBINES

A **turbine** is a device in which work is developed as a result of a gas or liquid passing through a set of blades attached to a shaft free to rotate.

Turbines are widely used in vapor power plants, gas turbine power plants, and aircraft engines. In these applications, superheated steam or a gas enters the turbine and expands to a lower exit pressure as work is developed.



- When gases are under consideration, changes in potential energy are negligible, as is the inlet kinetic energy. Often, the exit kinetic energy is neglected, and any heat rejection from the turbine is undesirable and is commonly small.

- We therefore normally assume that a turbine process is adiabatic, and the work output in this case reduces to the decrease in enthalpy from the inlet to exit states.
- For a turbine at steady state the mass and energy rate balances reduce to give

$$0 = \frac{\dot{Q}_{cv}}{\dot{m}} - \frac{\dot{W}_{cv}}{\dot{m}} + (h_1 - h_2) + \cancel{\frac{(V_1^2 - V_2^2)}{2}} + g(\cancel{z_1 - z_2})$$

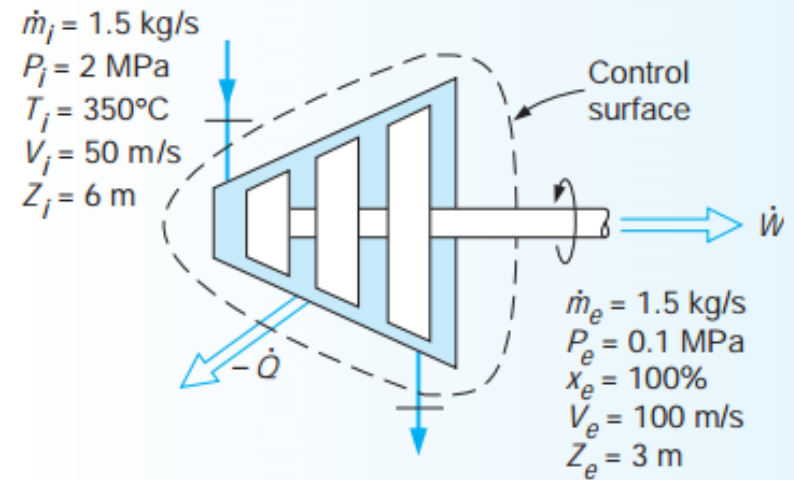
$$\frac{\dot{W}_{cv}}{\dot{m}} = (h_1 - h_2)$$

- In the following example, however, we include all the terms in the first law and study their relative importance.

Example

The mass rate of flow into a steam turbine is 1.5 kg/s, and the heat transfer from the turbine is 8.5 kW. The following data are known for the steam entering and leaving the turbine. Determine the power output of the turbine.

	Inlet Conditions	Exit Conditions
Pressure	2.0 MPa	0.1 MPa
Temperature	350°C	
Quality		100%
Velocity	50 m/s	100 m/s
Elevation above reference plane	6 m	3 m
$g = 9.8066 \text{ m/s}^2$		

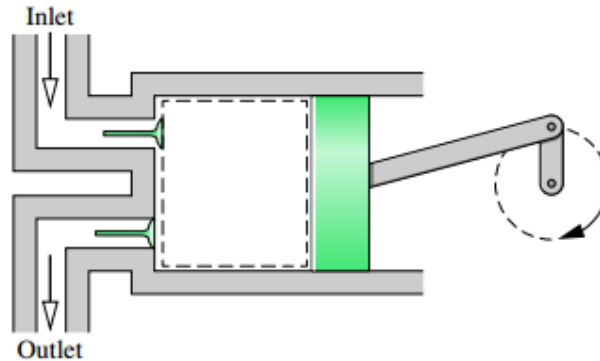


3. COMPRESSORS AND PUMPS

Compressors are devices in which work is done on a *gas* passing through them in order to raise the pressure.

In **pumps**, the work input is used to change the state of a *liquid* passing through.

- The mass and energy rate balances reduce for compressors and pumps at steady state, as for the case of turbines considered previously.
- For compressors, the changes in specific kinetic and potential energies from inlet to exit are often small relative to the work done per unit of mass passing through the device.
- Heat transfer with the surroundings is frequently a secondary effect in both compressors and pumps



Example

Air enters a compressor operating at steady state at a pressure of 1 bar, a temperature of 290 K, and a velocity of 6 m/s through an inlet with an area of 0.1 m². At the exit, the pressure is 7 bar, the temperature is 450 K, and the velocity is 2 m/s. Heat transfer from the compressor to its surroundings occurs at a rate of 180 kJ/min. Employing the ideal gas model, calculate the power input to the compressor, in kW.

4. HEAT EXCHANGERS

Devices that transfer energy between fluids at different temperatures by heat transfer modes such as conduction, convection and, radiation are called ***heat exchangers***. common type of heat exchanger is

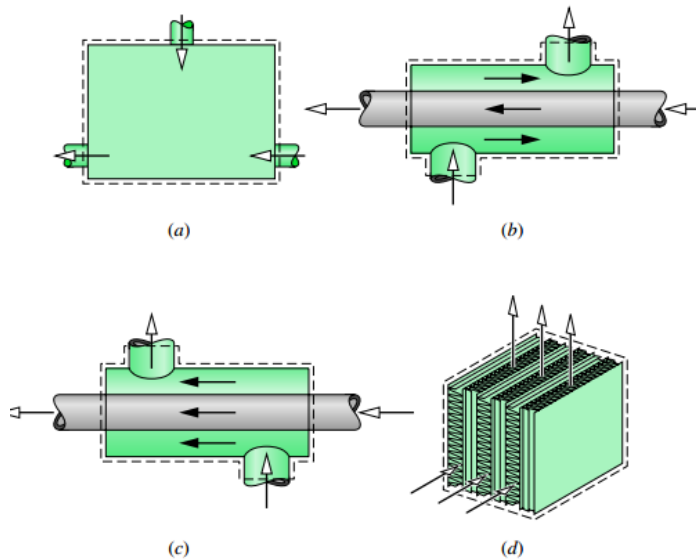


Figure: Common heat exchanger types. (a) Direct contact heat exchanger. (b) Tube-within-a-tube counter flow heat exchanger. (c) Tube-within-a-tube parallel flow heat exchanger. (d) Cross-flow heat exchanger.

- The only work interaction at the boundary of a control volume enclosing a heat exchanger is flow work at the places where matter enters and exits, so the term of the energy rate balance can be set to zero.
- Although high rates of energy transfer may be achieved from stream to stream, the heat transfer from the outer surface of the heat exchanger to the surroundings is often small enough to be neglected.
- In addition, the kinetic and potential energies of the flowing streams can often be ignored at the inlets and exits.

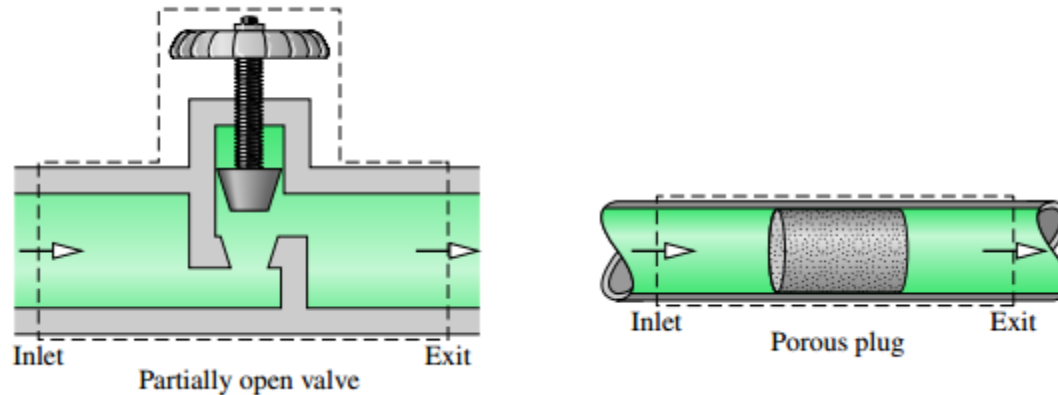
Example

Steam enters the condenser of a vapor power plant at 0.1 bar with a quality of 0.95 and condensate exits at 0.1 bar and 45°C. Cooling water enters the condenser in a separate stream as a liquid at 20°C and exits as a liquid at 35°C with no change in pressure. Heat transfer from the outside of the condenser and changes in the kinetic and potential energies of the flowing streams can be ignored. For steady-state operation, determine

- I. the ratio of the mass flow rate of the cooling water to the mass flow rate of the condensing stream.
- II. the rate of energy transfer from the condensing steam to the cooling water, in kJ per kg of steam passing through the condenser

5. THROTTLING DEVICES

A significant reduction in pressure can be achieved simply by introducing a restriction into a line through which a gas or liquid flows. This is commonly done by means of a partially opened valve or a porous plug, as illustrated in Figure.



For a control volume enclosing such a device, the mass and energy rate balances reduce at steady state to

$$0 = \dot{m}_1 - \dot{m}_2$$

$$0 = \dot{Q}_{cv} - \dot{W}_{cv}^0 + \dot{m}_1 \left(h_1 + \frac{V_1^2}{2} + gz_1 \right) - \dot{m}_2 \left(h_2 + \frac{V_2^2}{2} + gz_2 \right)$$

- There is usually no significant heat transfer with the surroundings and the change in potential energy from inlet to exit is negligible. With these idealizations, the mass and energy rate balances combine to give

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

- Although velocities may be relatively high in the vicinity of the restriction, measurements made upstream and downstream of the reduced flow area show in most cases that the change in the specific kinetic energy of the gas or liquid between these locations can be neglected.
- With this further simplification, the last equation reduces to

$$h_1 = h_2$$

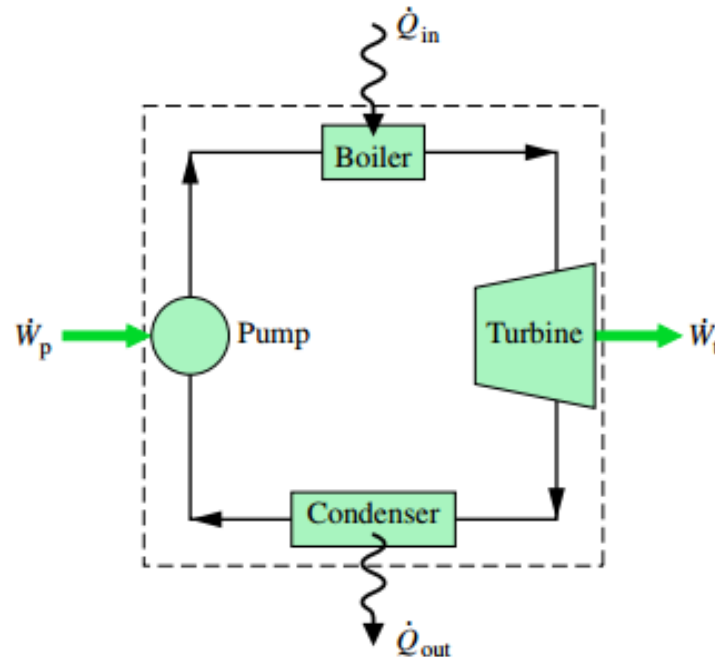
- When the flow through a valve or other restriction is idealized in this way, the process is called a ***throttling process***

Example

- A supply line carries a two-phase liquid–vapor mixture of steam at 20 bars. A small fraction of the flow in the line is diverted through a throttling calorimeter and exhausted to the atmosphere at 1 bar. The temperature of the exhaust steam is measured as 120°C. Determine the quality of the steam in the supply line.

6. SYSTEM INTEGRATION

- Thus far, we have studied several types of components selected from those commonly seen in practice.
- These components are usually encountered in combination, rather than individually.
- The simple power plant shown in Figure. This system consists of four components in series, a turbine-generator, condenser, pump, and boiler. So the combination of this components called system integration



Example

Consider the simple steam power plant, as shown in Figure below. The following data are for such a power plant

Location	Pressure	Temperature or Quality
Leaving boiler	2.0 MPa	300°C
Entering turbine	1.9 MPa	290°C
Leaving turbine, entering condenser	15 kPa	90%
Leaving condenser, entering pump	14 kPa	45°C
Pump work = 4 kJ/kg		

Determine the following quantities per kilogram flowing through the unit:

- Heat transfer in the line between the boiler and turbine.
- Turbine work.

c. Heat transfer in the condenser.

d. Heat transfer in the boiler.

