

CHAPTER 3: First Law of Thermodynamics

3.1 Concept of Internal Energy

We have noted in chapter 1 that the two most common modes of energy exchanged by a thermodynamic system and its surroundings are work and heat. The interconvertibility between these two forms of energy was first demonstrated by the British scientist James P. Joule during 1840s by a series of carefully executed experiments. The experimental setup he used is shown as a schematic in fig. 3.1. Known quantities of a set of fluids (water, oil, and mercury) were placed in an

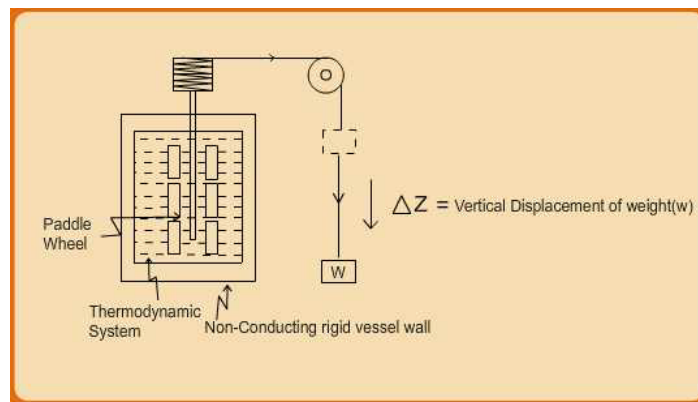


Fig. 3.1 Schematic of Joule's Experimental System

insulated, rigid vessel and stirred by means of rotating shaft provided with vanes. The amounts of work done on the fluid by the stirrer were measured in terms that needed to lower or raise a weight, and the resultant change in the temperature of the fluid was recorded. The key observation made by Joule was that for each fluid a *fixed* amount of work was required per unit mass for every degree of temperature rise caused by the rotating paddle wheel. Further, the experiments showed that the temperature of the fluid could be restored to its initial value by the transfer of heat by bringing it in contact with a cooler object. These experimental findings demonstrated for the first time that inter-convertibility exists between work and heat, and therefore the latter was also a form of energy.

Joule's observation also provided the basis for postulation of the concept of *internal energy* (introduced briefly in section 1.3). Since work and heat are distinctly different forms of energy, how is it possible to convert one into another? The question can be answered if one assumes that although these two types of energies are distinct in *transit* across a thermodynamic system boundary, they must eventually be stored within a thermodynamic system in a common

form. That common form is the so-called internal energy. As we have already discussed in section 1.3, such a form of energy can only repose at the microscopic level of atoms and molecules, essentially in the form of translational, vibrational and rotational energies. To this may be added the potential energy of intermolecular interactions (as introduced in section 2.2). On a sub-molecular scale energy is associated with the electrons and nuclei of atoms, and with bond energy resulting from the forces holding atoms together as molecules. With these considerations one is in a position to rationalize the observation that while a system may receive energy in the form of work done on it, it may part with it also in the form of heat to another body or surroundings and be restored to its state prior to receipt of work. This is possible as in the interim between these two processes all energy may be stored in the form of internal energy.

As may be evident from the foregoing discussion, the addition of heat or work from an external source can lead to enhancement of the microscopic form of systemic (internal) energy. As also noted in chapter 1 the terminology “internal” is applied mainly to distinguish it from the mechanical potential and kinetic energies that a thermodynamic system may also possess by virtue of its position and velocity with respect to a datum. The latter two may then be thought of as “external” forms of energy.

It is important to note that like other intensive, macroscopic variables such as pressure, temperature, mass or volume, internal energy is a *state variable* as it is wholly dependent on the energy states that its atoms / molecules. Thus any change in the (say, specific) internal energy due to a process would only depend on the initial and final states, and not on the path followed during the change. Thus as for changes in P, V or T, one may write:

$$\int_{U_1}^{U_2} dU = \Delta U = U_2 - U_1$$

However, unlike P, V, T or mass, U is not a directly measurable property. Besides, in common with potential and kinetic energies, no absolute values of internal energy are possible. However, this is not of particular significance as in thermodynamic processes one is always interested in *changes* in energies rather than their absolute values

3.2 The First Law of Thermodynamics

The empirical conclusion that heat and internal energy belong to the general category of energies, help extending the law of conservation of mechanical energy, which states that potential and kinetic energies are fully inter-convertible. As already discussed in chapter 1, a thermodynamic system may possess any other forms of energy such as surface energy, electrical energy, and magnetic energy, etc. Thus one may arrive at an extended postulate that all forms of energies are inter-convertible. This constitutes the basis of the *First Law of Thermodynamics*, which may be stated as follows:

Energy can neither be destroyed nor created, when it disappears in one form it must re-appear at the same time in other forms.

It must be said that there is no *formal* proof of the first law (or indeed of other laws of thermodynamics) is possible, but that no evidence have been found to date that violates the principle enunciated by it.

For any thermodynamic process, in general one needs to account for changes occurring both within a system as well as its surroundings. Since the two together forms the “universe” in thermodynamic terms, the application of the first law to a process leads to the following mathematical form:

$$\Delta(\text{Total energy of the universe}) = 0$$

$$\Delta(\text{Total energy of the system}) + \Delta(\text{Total energy of the surroundings}) = 0$$

Where $\Delta \equiv$ finite change occurring during the thermodynamic process

3.2 Application of the First Law to Closed Systems

In general, a thermodynamic system in its most complex form may be multi-component as well as multiphase in nature, and may contain species which react chemically with each other. Thermodynamic analysis tends to focus dominantly on the energy changes occurring within such a thermodynamic system due to change of state (or vice versa), and therefore it is often convenient to formulate the first law specifically for the system in question. Here we focus on closed systems, i.e., one that does not allow transfer of mass across its boundary. As already

pointed out work and heat may enter or leave such a system across its boundary (to and fro with respect to the surrounding) and also be stored in the common form of internal energy. Since in a system may also possess potential and kinetic energies, one may reframe the first law as follows.

Using the notations U, E_K, E_P for specific internal, kinetic and potential energies, respectively:

$$\Delta[U^{total} + E_{kinetic}^{total} + E_{potential}^{total}]_{system} = \text{Total energy input to system in all forms}$$

If the energy transfer across the system boundary takes place only the form of work and heat:

$$\Delta[U^{total} + E_{kinetic}^{total} + E_{potential}^{total}]_{system} = Q^{total}(\text{heat input}) + W^{total}(\text{work input})$$

The above relation may be written per unit mass / mole of closed system, i.e.,:

$$\Delta U + \Delta E_K + \Delta E_P = Q + W$$

The above equation may also be written in a differential form:

$$dU + dE_K + dE_P = \delta Q + \delta W \quad \dots(3.1)$$

If there is no change in potential and kinetic energies for the system or it is negligible – as is usually true for most thermodynamic systems of practical interest – the above equation reduces to:

$$dU = \delta Q + \delta W \quad \dots(3.2)$$

One of the great strengths of the mathematical statement of the first law as codified by eqn. 3.2 is that it equates a state variable (U) with two path variables (Q, W). As a differentiator we use the symbol δ to indicate infinitesimal work and heat transfer (as opposed to d used state variables). The last equation potentially allows the calculation of work and heat energies required for a process, by simply computing the change in internal energy. As we shall see later (chapters. 4 & 5) changes in internal energy can be conveniently expressed as functions of changes in state properties such as T, P and V .

In the above equation the term δW represents any form of work transfer to or from the system. In many situations of practical interest the thermodynamic work for closed systems is typically the PdV work (eqn. 1.6). Hence in such cases one may reframe eqn. 3.2 as follows:

$$dU = \delta Q + \delta W = \delta Q - \int_{V_1}^{V_2} PdV \quad \dots(3.3)$$

In keeping with the definition of work above, we adopt the following convention:

$W > 0$, if work is done on system

$W < 0$, if work is done by system

$Q > 0$, for heat addition to system

$Q < 0$, for heat removal from system

The process of change in a thermodynamic system may occur under various types of constraints, which are enlisted below:

- Constant pressure (*isobaric*)
- Constant volume (*isochoric*)
- Constant temperature (*isothermal*)
- Without heat transfer (*adiabatic*)

The mathematical treatment of each of these processes is presented below.

For a constant pressure process (fig. 3.2), we may write:

$$\delta Q = dU + PdV$$

$$\delta Q = d(U + PV)$$

$$\delta Q = d(U + PV)$$

$$\text{or } \delta Q = dH$$

$$\text{where, } H = U + PV$$

The term H is termed *enthalpy*. It follows that like U , H is also a state variable. On integrating the differential form of the equation above one obtains for the process:

$$\int_1^2 \delta Q = \int_1^2 dH$$

$$\text{Or: } Q = \Delta H \quad \dots(3.4)$$

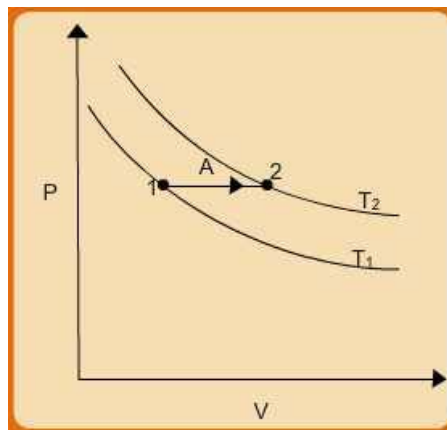


Fig. 3.2 Schematic of an Isobaric Path

On the other hand if the process occurs under isochoric (const. V) conditions (shown in fig. 3.3) the first law leads to:

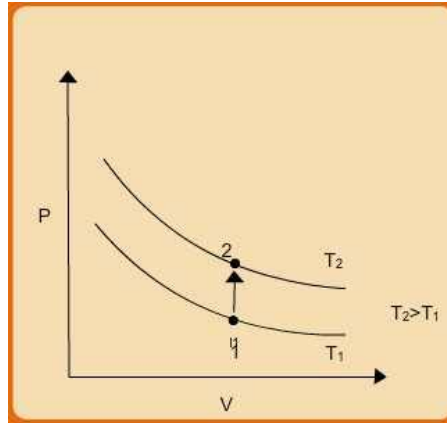


Fig. 3.3 Schematic of an Isochoric Path

$$\delta Q = dU$$

$$\int_1^2 \delta Q = \int_1^2 dH$$

$$Q = \Delta U \quad \text{..(3.5)}$$

We have already seen that a body can retain heat in the form of internal energy. This gives rise to the concept of heat capacity C and is mathematically defined as:

$$C \equiv \frac{\delta Q}{dT}$$

It follows that using eqns. 3.4 and 3.5 two types of heat capacity may be defined:

- Constant pressure heat capacity C_p such that:

$$C_p = \frac{\delta Q}{dT} = \left(\frac{\partial H}{\partial T} \right)_p \quad \text{..(3.6)}$$

- Constant volume heat capacity C_v such that:

$$C_v = \frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T} \right)_v \quad \text{..(3.7)}$$

Thus, using eqns. (3.6) and (3.7) one may rewrite eqns. (3.4) and (3.5) as follows:

$$Q = \Delta H = \int_{T_1}^{T_2} C_p dT \quad (\text{At const P.}) \quad \text{..(3.8)}$$

$$Q = \Delta U = \int_{T_1}^{T_2} C_V dT \quad (\text{At const V.}) \quad \dots(3.9)$$

With the addition of heat to a system, the translation, vibrational and rotational (as well as subatomic) energies of the molecules are enhanced and so it may be expected that the specific heats would be dependent on temperature. On the other hand when substances are compressed intermolecular interactions begin to contribute to internal energy (as hence to enthalpy) and therefore specific heats are rendered pressure dependent. For the case of ideal gases, however, the specific heats are independent of pressure as there are no intermolecular interactions; they are only temperature dependent. Values of specific heats of ideal gases (*ig*), say at constant pressure, are available from experimental measurements and are typically expressed in the form of polynomials such as:

$$\frac{C_P^{ig}}{R} = A + BT + CT^2 + \frac{D}{T^2} \quad \dots(3.10)$$

Where, A, B, C and D are characteristic constants for a substance, and R is the universal gas constant. Values of the constants in eqn. (3.10) are readily available for a large number of pure substances (see [Appendix III](#) for values of select gases). Fig. 3.4 shows typical dependence of const, pressure specific heat for select substances with temperature.

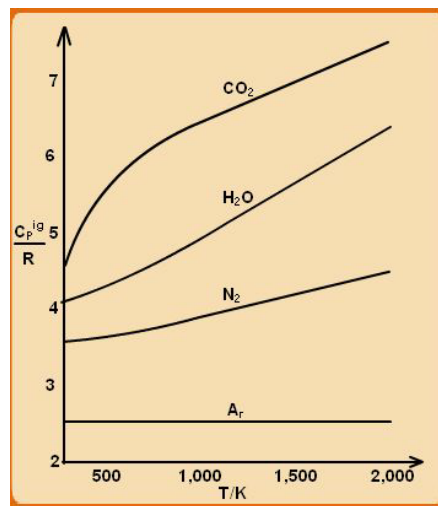


Fig. 3.4 Variation of C_P^{ig}/R vs. Temperature (Source: J. M Smith, H.C. Van Ness, M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, 6th ed., McGraw-Hill, 2001)

Values of the coefficients of similar specific heat capacity polynomials for liquids and solids are available elsewhere (see for example, J.M. Smith, H.C. Van Ness and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, 2001).

Applications to Ideal Gases

The other two types of thermodynamic processes – *isothermal and adiabatic* – in closed systems are conveniently understood by applying the first law to a system comprised of an ideal gas. For such a case the relationship between U and H may be rewritten using the EOS:

$$H = U + PV = U + RT$$

$$\text{Or: } H - U = RT$$

Since both H and U are only temperature dependent for ideal gases we write:

$$\frac{dH}{dT} - \frac{dU}{dT} = R$$

Now using eqns. 3.6 and 3.7 it follows that:

$$C_p - C_v = R \quad \text{..(3.11)}$$

(It may be noted that since the molar volume V is relatively small for both liquids and solids, one may write: $H \approx U$; hence: $C_p \approx C_v$).

Let us now consider the relationships that obtain for an isothermal process for an ideal gas. Using eqn. 3.2, since $dU = 0$:

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

$$\text{Or, } Q = -W$$

If we consider only P-V work, the work term is calculable if the process is carried out reversibly, as the ideal gas EOS relate the P and V at all points of change, hence:

$$W = -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} \left(\frac{RT}{V} \right) dV = RT \ln \frac{V_1}{V_2} = RT \ln \frac{P_2}{P_1} \quad \text{..(3.12)}$$

Thus:

$$Q = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2} \quad \text{..(3.13)}$$

Example 3.1

A gas initially at 1 MPa, 500°C is contained in a piston-cylinder arrangement of initial volume of 0.1 m³. The gas expanded isothermally to a final pressure of 100 kPa. Determine the work.

(Click for solution)

$$\text{For isobaric process: } Q = \Delta H = \int C_p dT; W = -\int_{V_1}^{V_2} P dV = -P(V_2 - V_1) = -R(T_2 - T_1) \quad \text{..(3.14)}$$

For *adiabatic* process $dQ = 0$

Hence : $dU = \delta W$

$$\text{Or : } C_v dT = -P dV = -\frac{RT}{V} dV$$

$$\frac{dT}{T} = -\frac{R}{C_v} \frac{dV}{V} \quad \text{..(3.15)}$$

The ratio of heat capacities is defined as:

$$\gamma = C_p / C_v$$

Or:

$$\gamma = \frac{C_v + R}{C_v} = 1 + \frac{R}{C_v} \quad \text{..(3.16)}$$

On integrating eqn. 3.15 and using the relationship provided by eqn. 3.16, the following set of results may be derived easily:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \quad \text{..(3.17)}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \quad \text{..(3.18)}$$

$$\text{and } P_1 V_1^\gamma = P_2 V_2^\gamma = PV^\gamma = \text{const.} \quad \text{..(3.19)}$$

Further: $dW = dU = C_v dT$

Or $W = dU = C_v dT$

Since, $W = -\int P dV$

Using eqn. 3.19 in the expression for work in the last equation:

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \quad \text{..(3.20)}$$

Or:

$$W = \frac{P_1 V_1}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] = \frac{RT_1}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad \text{..(3.21)}$$

All the above processes discussed can be captured in the form of a single P - V relation, which is termed a *polytropic* equation as it can be reduced to yield all forms of processes. The polytropic relations are written by generalizing eqns. 3.17 – 3.19, as follows:

$$PV^\delta = \text{constant} \quad \text{..(3.22)}$$

$$TV^{\delta-1} = \text{constant} \quad \text{..(3.23)}$$

$$TP^{(1-\delta)/\delta} = \text{constant} \quad \text{..(3.24)}$$

The schematic of polytropic process is shown in fig. 3.5.

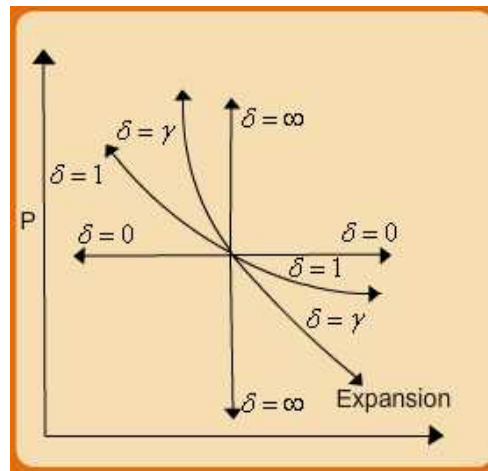


Fig. 3.5 Schematic of Polytropic Processes

As may be seen the various values of δ reproduce the isothermal, isochoric, isobaric and adiabatic processes. In line with eqn. 3.21, for such the generalized expressions for work and heat transfer may be shown to be:

$$W = \frac{RT_1}{\delta - 1} \left[\left(\frac{P_2}{P_1} \right)^{(\delta-1)/\delta} - 1 \right] \quad \text{..(3.25)}$$

Further:

$$Q = \frac{(\delta - \gamma) RT_1}{(\delta - 1)(\gamma - 1)} \left[\left(\frac{P_2}{P_1} \right)^{(\delta-1)/\delta} - 1 \right] \quad \text{..(3.26)}$$

Example 3.2

Helium gas expands from 125 kPa, 350 K and 0.25 m³ to 100 kPa in a polytropic process with $\delta = 1.667$. How much work does it give out?

[\(Click for solution\)](#)

3.3 Application of the First Law to Open Systems

While the last section addressed processes occurring in closed systems, the wider application of the first law involves formulating the energy balance differently in order to accommodate the fact that most thermodynamic systems, i.e., equipments, in continuous process plants are essentially open systems: they allow mass transfer across their boundaries (i.e., through inlet and outlet). Examples include pumps, compressors, reactors, distillation columns, heat exchangers etc. Since such open systems admit both material and energy transfer across their boundaries the thermodynamic analysis necessarily involves both mass and energy balances to be carried out together. Also such systems may in general operate under both steady (during normal plant operation) and unsteady states (say during startup and shutdown). As we will see the former state is a limiting case of the more general situation of unsteady state behavior.

Mass Balance for Open Systems:

For generality consider an open system with which has multiple inlets (1, 2) and outlets (3, 4). The volume enclosed by the physical boundary is the *control volume* (CV). The general mass balance equation for such a system may be written as:

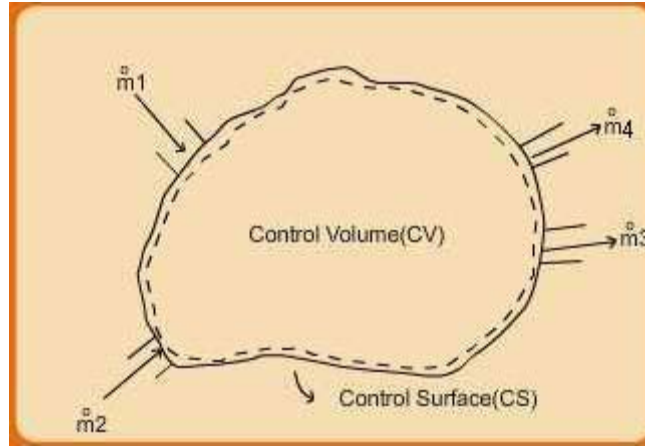


Fig. 3.6 Schematic of an open system

$$\frac{dm_{cv}}{dt} = \sum_{inlet} \dot{m} - \sum_{outlet} \dot{m} \quad ..(3.27)$$

The mass flow rate \dot{m} is given by:

$$\dot{m} = \rho u A \quad ..(3.28)$$

Where, ρ = fluid density; u = fluid velocity; and A = aperture cross-sectional area

The first term on the left side of the eqn. (3.27) denotes sum of all flow rates over all inlets, while the second term corresponds to the summation over all outlet flow rates. For the system shown in fig. 3.5 the eqn. 3.27 may be written as:

$$\frac{dm_{cv}}{dt} = \dot{m}_1 + \dot{m}_2 - \dot{m}_3 - \dot{m}_4 \quad ..(3.28)$$

The last equation may be reframed in a general way as follows:

$$\frac{dm_{cv}}{dt} + \Delta(\dot{m})_{fs} = 0 \quad ..(3.29)$$

Where the symbol $\Delta \equiv$ outlet-inlet; and the subscript fs stands for "flow streams".

Equation 3.29 may be recast as:

$$\frac{dm_{cv}}{dt} + \Delta(\rho u A)_{fs} = 0 \quad ..(3.30)$$

The above equation simplifies under steady flow conditions as the accumulation term for the control volume, i.e., $\frac{dm_{cv}}{dt} = 0$

In such a case for the simplest case of a system with one inlet and outlet (say: 1 and 2 respectively), which typically represents the majority of process plant equipments, the mass balance equation reduces to:

$$\dot{m} = \text{constant} \quad \dots(3.31)$$

$$\text{Or: } \rho_1 u_1 A_1 = \rho_2 u_2 A_2 \rightarrow u_1 A_1 / V_1 = u_2 A_2 / V_2$$

Where V = specific volume

Energy Balance for Open Systems:

Consider the schematic of an open system as shown in fig. 3.7. For simplicity we assume one

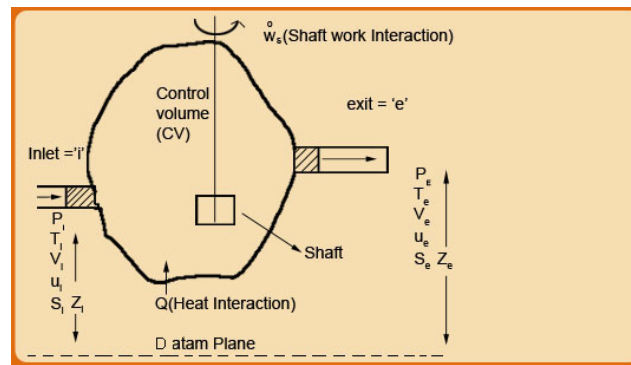


Fig. 3.7 Schematic of an open system showing flow and energy interactions

inlet and one exit ports to the control volume. The thermodynamic states at the inlet i and exit e are defined by the P , V , T , u (average fluid velocity across the cross section of the port), and Z , the height of the port above a datum plane. A fluid element (consider an unit mole or mass) enters the CV carrying internal energy, kinetic and potential energies at the inlet conditions (P_i , T_i , with molar volume as V_i) and leaves values of these energies at the exit state conditions (P_e , T_e , with molar volume as V_e). Thus the total specific energy of the fluid at the two ports corresponds to

the sum of specific internal, potential and kinetic energies, given by: $U + \frac{u^2}{2} + gZ$. In addition,

the CV exchanges heat with the surroundings at the rate \dot{Q} , and say a total work (in one or more

forms) at the rate of \dot{W}_{total}

In the schematic we, however, have shown a specific work form, *shaft work*, that is delivered *to* or *by* the system by means of rotatory motion of a paddle wheel which, as we will see later in the section, is implicated in many typical process plant units. As with material balance one may write a total energy balance equation for the control volume as follows:

$$\frac{d(mU)_{cv}}{dt} = \left[\left(U + \frac{1}{2}(u^2) + zg \right) \dot{m} \right]_i - \left[\left(U + \frac{1}{2}(u^2) + zg \right) \dot{m} \right]_e + \dot{Q} + \dot{W}_{total}$$

Or:

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[\left(U + \frac{1}{2}(u^2) + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_{total} \quad ..(3.32)$$

The general total work term should include all forms of work. We draw the reader's attention to the fact that the total work interaction also should include that needed to push fluid into the CV as well as that implicated in pushing it out of CV. The fluid state at the inlet or exit is characterized by a set of state properties, U, V, H, etc. Consider a unit mass (or mole) of fluid entering the CV. This fluid element obviously needs to be "pushed" by another that follows it so as to make the formed enter the CV. In essence a fluid element of (specific) volume V is pushed into the CV at a pressure P. This is akin to a P-V form of work (as in the case of a piston-in-a-cylinder system) that is done on the CV and so may be quantified as $-P_i V_i$. The same considerations apply at the exit in which case in pushing out a similar fluid element at exit conditions, i.e., $-P_e V_e$. Thus, eqn. 3.32 may be rewritten as follows:

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[\left(U + \frac{1}{2}(u^2) + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W} - [PV \dot{m}]_i + [PV \dot{m}]_e \quad ..(3.33)$$

Where, $\dot{W}_{total} = \dot{W} - [PV \dot{m}]_i + [PV \dot{m}]_e$

The term \dot{W} represents sum of *all other* forms of work associated with the process occurring within the CV. This residual work term may include the shaft work, P-V work resulting from expansion or contraction of the CV, electrical work, and so on. As the last two work terms on the left side of the eqn. 3.33 are associated with the flow streams we may rewrite the equation as follows:

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[\left(U + \frac{1}{2}(u^2) + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W} - \Delta [PV \dot{m}]_{fs} \quad \text{..(3.34)}$$

On rearranging:

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[\left\{ (U + PV) + \frac{u^2}{2} + zg \right\} \dot{m} \right]_{fs} = \dot{Q} + \dot{W} \quad \text{..(3.35)}$$

$$\text{Or: } \frac{d(mU)_{cv}}{dt} + \Delta \left[\left\{ H + \frac{u^2}{2} + zg \right\} \dot{m} \right]_{fs} = \dot{Q} + \dot{W} \quad \text{..(3.36)}$$

It may be noted that eqn. 3.34 assumes that the CV is fixed in space and therefore no overall potential of kinetic energy terms depicting these mechanical energies for the control volume is included. This, of course, is valid for all process plant applications. In addition, For many cases of practical importance (though not all) in a chemical plant the kinetic and potential energy changes between the inlet and exit streams may not be significant, whence the last equation may be simplified as: an equipment may be neglected; hence:

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[H \dot{m} \right]_{fs} = \dot{Q} + \dot{W} \quad \text{..(3.37)}$$

Further, for the special case where the only shaft work is involved, the above equation may be simplified to:

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[H \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_s \quad \text{..(3.38)}$$

For *steady state* applications the eqn. 3.34 reduces to:

$$\Delta \left[\left\{ H + \frac{u^2}{2} + zg \right\} \dot{m} \right]_{fs} = \dot{Q} + \dot{W} \quad \text{..(3.39)}$$

Further, if the kinetic and potential energy changes associated with the flow streams are insignificant, it follows that:

$$\Delta \left[H \dot{m} \right]_{fs} = \dot{Q} + \dot{W} \quad \text{..(3.40)}$$

Since under steady state \dot{m} is constant we may write:

$$\Delta H = Q + W \quad \text{..(3.41)}$$

Where Q and W denote the work and heat interactions per unit mass of mole of fluid flowing through the system flowing through system. Once again if W_s is the only form of work interaction between the system and the surrounding then:

$$\Delta H = Q + W_s \quad \text{..(3.42)}$$

Examples of process plant units to which eqn. 3.42 applies are: *pumps, compressors, turbines, fans, blowers*, etc. In all cases a rotatory part is used exchange work between the system and surrounding.

Example 3.3

A chiller cools liquid water (Sp. Ht = 4.2 J/gmK) for air-conditioning purposes. Assume 2.5 kg/s water at 20°C and 100 kPa is cooled to 5°C in a chiller. How much heat transfer (kW) is needed?

[\(Click for solution\)](#)

Example 3.4

A piston-cylinder assembly contains 0.1 kg wet steam of quality 0.75 at 100 kPa. If 150 kJ of energy is added as heat while the pressure of the steam is held constant determine the final state of steam.

[\(Click for solution\)](#)

Example 3.5

An adiabatic compressor operating under steady-state conditions receives air (ideal gas) at 0.1 MPa and 300 K and discharges at 1 MPa. If the flow rate of air through the compressor is 2 mol/s, determine the power consumption of the compressor. Constant pressure specific heat for air = 1kJ/kg.

[\(Click for solution\)](#)

Example 3.6

An insulated piston-cylinder system has air at 400kPa & 600K. Through an inlet pipe to the cylinder air at certain temperature T(K) and pressure P (kPa) is supplied reversibly into the

cylinder till the volume of the air in the cylinder is 4 times the initial volume. The expansion occurs isobarically at 400kPa. At the end of the process the air temperature inside the cylinder is 450K. Assume ideal gas behaviour compute the temperature of the air supplied through the inlet pipe.

[\(Click for solution\)](#)

3.4 Measurement of Enthalpy and Internal Energy using Flow Calorimeter

The use of the first law for open or closed systems necessitates the experimental determination (or, estimation from thermodynamic relations) of internal energy and enthalpy, both being state properties. The flow calorimeter (fig. 3.8), readily allows measurement of enthalpy, which in turn can be used to compute the internal energy at the same conditions of (say) temperature and pressure. The fluid whose properties are to be measured is pumped through a constant temperature bath so that it attains a desired temperature (say T_1) prior to entry into the vessel provided with an electric heater. The corresponding pressure (P_1) may also be recorded. Heat is next provided to the passing fluid at a pre-determined and fixed rate over a period of time until the temperature and pressure at the exit of the vessel attains steady values (say, T_2 , & P_2). At such a condition the calorimeter is under steady state, hence eqn. 3.41 may be applied to the heating vessel. Since there is no work transfer of any kind, the resultant energy balance yields:

$$\Delta H = Q \quad \dots(3.40)$$

$$\text{Or: } H_2 - H_1 = Q$$

$$\text{So: } H_2 = H_1 + Q \quad \dots(3.41)$$

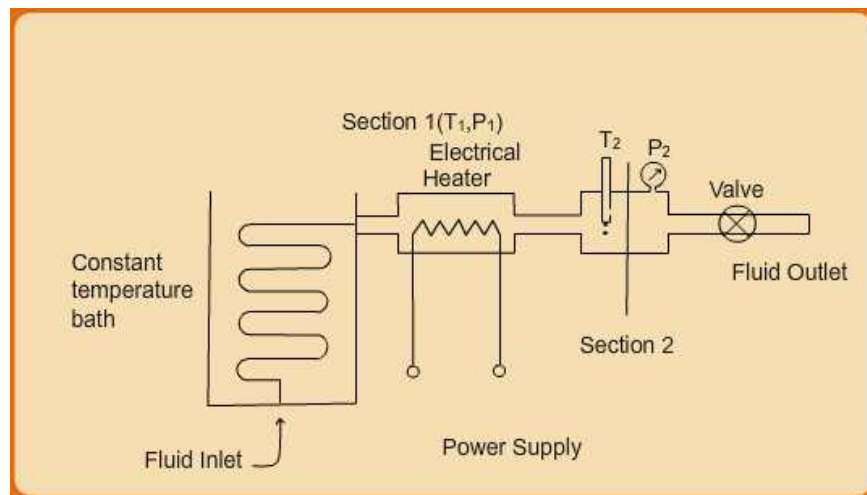


Fig. 3.8 A schematic of a flow calorimeter

Clearly, if we chose the enthalpy H_1 to be a datum state and arbitrarily assign it a zero value, then:

$$H_2 = Q \quad \text{..(3.42)}$$

The last equation then allows one to uniquely determine the value of H_2 at any condition achieved at state 2 by applying a known quantity of heat through the electric heating system. The internal energy at the same state can next be determined using the relation:

$$U = H - PV \quad \text{..(3.42)}$$

Further we can measure the density (in terms of mass or mole) at the same state, and one may

$$\text{rewrite the last equation as: } U = H - P/\rho \quad \text{..(3.43)}$$

Thus using the above relations, U and H may be obtained experimentally at any P , T (and/or V) for any substance. The steam tables discussed at the concluding portion of section 2.1 constitutes such a tabulation of values of standard thermodynamic properties (saturation vapour pressure, internal energy, enthalpy (and entropy) of water obtained empirically over a wide range temperature and pressure.

Assignment-Chapter 3