

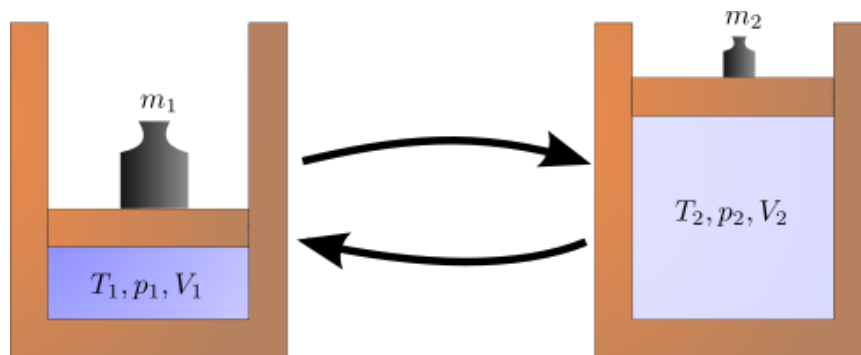
Thermodynamic

1. EQUILIBRIUM

Equilibrium is a word denoting a static condition, the absence of change. In thermodynamics it means not only the absence of change but the absence of any tendency toward change on a macroscopic scale. Thus a system at equilibrium exists under conditions such that no change in state can occur. Since any tendency toward change is caused by a driving force of one kind or another, the absence of such a tendency indicates also the absence of any driving force. Hence for a system at equilibrium all forces are in exact balance. Whether a change actually occurs in a system not at equilibrium depends on resistance as well as on driving force. Many systems undergo no measurable change even under the influence of large driving forces, because the resistance to change is very large.

2. THE REVERSIBLE PROCESS

A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions.



A reversible process:

- Ideal
- Is frictionless
- Traverses a succession of equilibrium states
- Is driven by forces whose imbalance is differential in magnitude
- Can be reversed at any point by a differential change in external conditions
- When reversed, retraces its forward path, and restores the initial state of system and surroundings

$$W = - \int_{V_i}^{V_f} P dV \quad (1.3)$$

Results for reversible processes in combination with appropriate efficiencies yield reasonable approximations of the work for actual processes.

Example 2.6

A horizontal piston/cylinder arrangement is placed in a constant-temperature bath. The piston slides in the cylinder with negligible friction, and an external force holds it in place against an initial gas pressure of 14 bar. The initial gas volume is 0.03 m^3 . The external force on the piston is reduced gradually, and the gas expands isothermally as its volume doubles. If the volume of the gas is related to its pressure so that the product PV^T is constant, what is the work done by the gas in moving the external force?

How much work would be done if the external force were suddenly reduced to half its initial value instead of being gradually reduced?

Solution 2.6

The process, carried out as first described, is mechanically reversible, and Eq. (1.3) is applicable. If $PV^T = k$, then $P = k/V^T$, and

$$W = - \int_{V_1^T}^{V_2^T} P dV^T = -k \int_{V_1^T}^{V_2^T} \frac{dV^T}{V^T} = -k \ln \frac{V_2^T}{V_1^T}$$

With $V_1^T = 0.03 \text{ m}^3$ $V_2^T = 0.06 \text{ m}^3$

and $k = PV^T = P_1 V_1^T = (14 \times 10^5)(0.03) = 42,000 \text{ J}$

$$W = -42,000 \ln 2 = -29,112 \text{ J}$$

The final pressure is

$$P_2 = \frac{k}{V_2^{\gamma}} = \frac{42,000}{0.06} = 700,000 \text{ Pa} \quad \text{or} \quad 7 \text{ bar}$$

In the second case, reduction of the initial force by half is followed by sudden expansion of the gas against a constant force equivalent to a pressure of 7 bar. Eventually, heat transfer returns the system to the same final equilibrium state as in the reversible process. Thus ΔV^T is the same as before, but the work accomplished is not given by Eq. (1.3). Rather, the work done against the external force equals the equivalent external pressure times the volume change:

$$W = -(7 \times 10^5)(0.06 - 0.03) = -21,000 \text{ J}$$

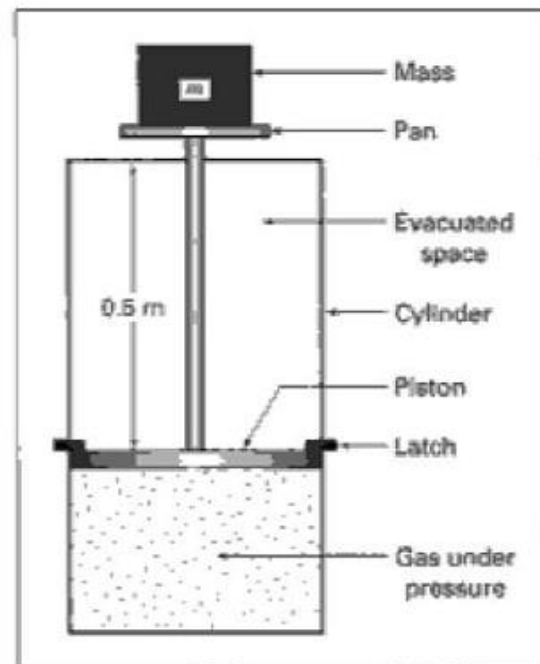
This process is clearly irreversible, and compared with the reversible process is said to have an efficiency of:

$$21,000/29,112 = 0.721 \quad \text{or} \quad 72.1\%$$

Example 2.7

The piston/cylinder arrangement shown in Fig. 2.4 contains nitrogen gas trapped below the piston at a pressure of 7 bar. The piston is held in place by latches. The space above the piston is evacuated. A pan is attached to the piston rod and a mass m of 45 kg is fastened to the pan. The piston, piston rod, and pan together have a mass of 23 kg. The latches holding the piston are released, allowing the piston to

Figure 2.4: Diagram for Ex. 2.7.



rise rapidly until it strikes the top of the cylinder. The distance moved by the piston is 0.5 m. The local acceleration of gravity is 9.8 m s^{-2} . Discuss the energy changes that occur because of this process.

Solution 2.7

This example illustrates the limited capacity of thermodynamics for analysis of irreversible nonflow processes. Let the gas alone be the system. By its basic definition, work done by the gas on the surroundings equals $\int P' dV'$, where P' is the pressure exerted by the gas on the piston. Because the expansion is very rapid, pressure gradients exist in the gas, and neither P' nor the integral can be evaluated. However, a return to Eq. (2.1) avoids the calculation of work. The energy change of the system (the gas) is ΔU_{sys}^t . In the surroundings the piston, rod, pan, and mass m change in potential energy and the piston, rod, and cylinder change in internal energy. With $Q = 0$, Eq. (2.1) is written:

$$\Delta U_{\text{sys}}^t + (\Delta U_{\text{surr}}^t + \Delta E_{P_{\text{surr}}}) = 0$$

where $\Delta E_{P_{\text{surr}}} = (45 + 23)(9.8)(0.5) = 333.2 \text{ N m}$

Therefore $\Delta U_{\text{sys}}^t + \Delta U_{\text{surr}}^t = -333.2 \text{ N m} = -333.2 \text{ J}$

Values for ΔU_{sys}^t and ΔU_{surr}^t cannot be determined.

Irreversible process: A process in which it is impossible to return both the system and surroundings to their original states.

The work of an irreversible process is calculated by a two-step procedure. First, W is determined for a mechanically reversible process that accomplishes the same change of state as the actual irreversible process. Second, this result is multiplied or divided by an efficiency to give the actual work. If the process produces work, the absolute value for the reversible process is too large and must be multiplied by efficiency. If the process requires work, the value for the reversible process is too small and must be divided by efficiency.

$$W_{\text{irr.}} = W_{\text{rev.}} \cdot \text{efficiency} \quad \text{if the process produces work}$$

$$W_{\text{irr.}} = W_{\text{rev.}} / \text{efficiency} \quad \text{if the process requires work}$$

3. CONSTANT-V AND CONSTANT-P PROCESSES

The energy balance for a homogeneous closed system of n moles is:

$$d(nU) = dQ + dW \quad (2.6)$$

where Q and W always represent total heat and work, whatever the value of n .

The work of a mechanically reversible, closed-system process is given by Eq. (1.2), here written:

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$$dW = -Pd(nV)$$

These two equations combine:

$$d(nU) = dQ - Pd(nV) \quad (2.8)$$

This is the general first-law equation for a mechanically reversible, closed-system process.

3.1 Constant-Volume Process

If the process occurs at constant total volume, the work is zero. Moreover, for closed systems the last term of Eq. (2.8) is also zero, because n and V are both constant. Thus,

$$dQ = d(nU) \quad (\text{const } V) \quad (2.9)$$

Integration yields:

$$Q = n \Delta U \quad (\text{const } V) \quad (2.10)$$

Thus for a mechanically reversible, constant-volume, closed-system process, the heat transferred is equal to the internal-energy change of the system.

3.2 Constant-Pressure Process

Solved for dQ , Eq. (2.8) becomes:

$$dQ = d(nU) + P d(nV)$$

For a constant-pressure change of state:

$$dQ = d(nU) + d(nPV) = d[n(U + PV)]$$

The appearance of the group $U + PV$, both here and in other applications. Thus, the mathematical (and only) definition of enthalpy is:

$$\boxed{H \equiv U + PV} \quad (2.11)$$

where H , U , and V are molar or unit-mass values. The preceding equation may now be written:

$$dQ = d(nH) \quad (\text{const } P) \quad (2.12)$$

Integration yields:

$$Q = n \Delta H \quad (\text{const } P) \quad (2.13)$$

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Thus for a mechanically reversible, constant-pressure, closed-system process, the heat transferred equals the enthalpy change of the system.

4. Enthalpy

Enthalpy is a measure of the total energy of a thermodynamic system. It includes the system's internal energy or thermodynamic potential (a state function), as well as its volume and pressure.

Since U , P , and V are all state functions, H as defined by Eq. (2.11) is also a state function. Enthalpy is defined for any system by mathematical expression as:

$$H = U + PV \quad (2.11)$$

U = internal energy

P = absolute pressure

V = system volume

The differential form of Eq. (2.11) is:

$$dH = dU + d(PV) \quad (2.14)$$

This equation applies whenever a differential change occurs in the system. Upon integration, it becomes an equation for a finite change in the system:

$$\Delta H = \Delta U + \Delta(PV) \quad (2.15)$$

Example 2.8

Calculate ΔU and ΔH for 1 kg of water when it is vaporized at the constant temperature of 100°C and the constant pressure of 101.33 kPa. The specific volumes of liquid and vapor water at these conditions are 0.00104 and $1.673 \text{ m}^3 \text{ kg}^{-1}$. For this change, heat in the amount of 2,256.9 kJ is added to the water.

Solution 2.8

We take the 1 kg of water as the system, because it alone is of interest, and imagine it contained in a cylinder by a frictionless piston which exerts a constant pressure of 101.33 kPa. As heat is added, the water evaporates, expanding from its initial to its final volume. Equation (2.13) as written for the 1-kg system is:

$$\Delta H = Q = 2,256.9 \text{ kJ}$$

By Eq. (2.15), $\Delta U = \Delta H - \Delta(PV) = \Delta H - P \Delta V$

Evaluate the final term:

$$\begin{aligned} P \Delta V &= 101.33 \text{ kPa} \times (1.673 - 0.001) \text{ m}^3 \\ &= 169.4 \text{ kPa m}^3 = 169.4 \text{ kN m}^{-2} \text{ m}^3 = 169.4 \text{ kJ} \end{aligned}$$

Then $\Delta U = 2,256.9 - 169.4 = 2,087.5 \text{ kJ}$