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.

The work of compression or expansion of a gas caused by the differential displacement of a piston in a cylinder.

$$dW = -PdV^t$$

The work done on the system is given by this equation only when certain characteristics of the reversible process are realized. The first requirement is that the system be no more than infinitesimally displaced from a state of internal equilibrium characterized by uniformity of temperature and pressure. The system then always has an identifiable set of properties, including pressure P. The second requirement is that the system be no more than infinitesimally displaced from mechanical equilibrium with its surroundings. In this event, the internal pressure P is never more than minutely out of balance with the external force, and we may make the substitution $F = PA$ that transforms Eq. (1.1) into Eq. (1.2). Processes for which these requirements are met are said to be mechanically reversible, and Eq. (1.2) may be integrated:

$$W = - \int_{V_1}^{V_2} PdV$$
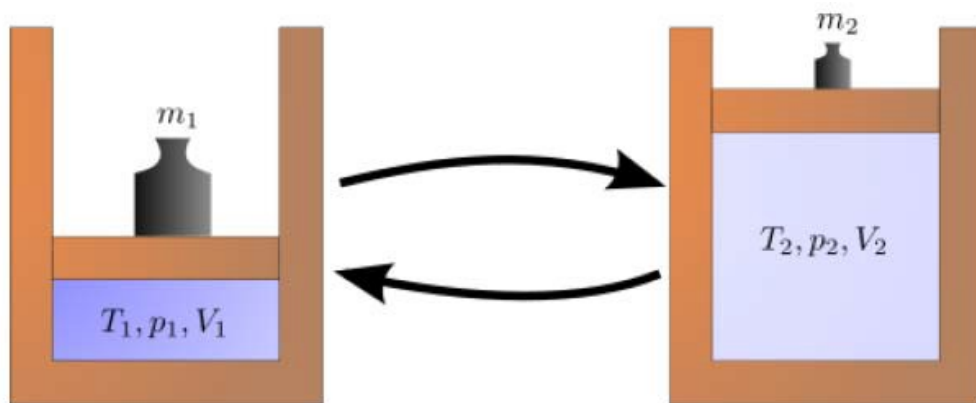
Irreversible process: A process in which it is impossible to return both the system and surroundings to their original states. The work of an irreversible process is calculated by a two-step procedure. First, W is determined for a mechanically reversible process that accomplishes the same change of state 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.

$W_{irr.} = W_{rev.} * efficiency$ if the process produces work

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

Example

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 the **14 bar**. The initial gas volume is **0.03 m³**. The external force on the piston is reduced gradually, and the gas expands isothermally as it **volume doubles**. If the volume of the gas is related to its pressure so that the **PV 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 the half its initial value instead of the being gradually reduced?

Solution

The process carried out as first described is mechanically reversible

$$w = -\int_{v_1}^{v_2} P dv$$

PV is constant and let say is equal K $\rightarrow \therefore PV = K \rightarrow$ $\therefore P = \frac{K}{V}$

$$K = P_1 V_1 \rightarrow K = 14 \times 10^5 \times 0.03 = 42000J$$

$$with\ v_1 = 0.03\ m^3 \qquad \rightarrow\ v_2 = 0.06\ m^3$$

$$W = -K \int_{v_1}^{v_2} \frac{dv}{V} = -Kln\frac{V_2}{V_1}$$

$$\therefore W = -42000ln2 = -29112J$$

The final pressure is $P_2 = \frac{K}{V_2} = \frac{42000}{0.06} = 700000\ Pa\ or\ 7\ bar$

In the second case the external forece was reduced to half $\therefore P = 7\ bar$

$$W = -(7 \times 10^5)(0.06 - 0.03) = -21000J$$

Were the efficiency of such processes known to be about 80%, we could Multiply the reversible work by this figure to get an estimate of the irreversible work, namely −23,290 J.

Enthalpy

Enthalpy appears in energy balances for flow processes as applied to heat exchangers, evaporators, distillation columns, pumps, compressors, turbines, engines, etc., for calculation of heat and work.

The tabulation of values of Q and W for the infinite array of possible processes is impossible. The intensive state functions, however, such as specific volume, specific internal energy, and specific enthalpy, are intrinsic properties of matter. Once determined, their values can be tabulated as functions of temperature and pressure for each phase of a particular substance for future use in the calculation of Q and W for any process involving that substance. Enthalpy equation can be write as

$$\boldsymbol{H = U + PV} \tag{1}$$

All terms of Eq. (1) must be expressed in the same units. The product PV has units of energy per mole or per unit mass, as does U; therefore H also has units of energy per mole or per unit mass. In the SI system the basic unit of pressure is the pascal ($=1$ N·m^{-2}), and that of molar volume is cubic meters per mol ($=1$ m^3·mol^{-1}). For the PV product we have 1 N·m·mol^{-1} = 1 J·mol^{-1}.

Because U, P, and V are all state functions, H as defined by Eq. (1) is also a state function. Like U and V, H is an intensive property of the system. The differential form of Eq. (1) is:

$$dH = dU + d(PV) \tag{2}$$

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

$$\Delta H = \Delta U + \Delta(PV) \tag{3}$$

Equations (1), (2), and (3) apply to a unit mass of substance or to a mole.

Example

Calculate ΔU and ΔH for 1 kg of water when vaporized at the constant tempreture of 373.15K (100 °C) and the constant pressure of 101.325 Pa. the specific volume of liquid or vapor water at these conditions are 0.00104 and 1.673 m³ kg⁻¹ respectively. For this change, heat in the amount of 2256.9 kJ is added to the water.

Solution

$$U = Q + w$$

$$dU = dQ + dw$$

$$dw = -dPV$$

$$dU = dQ - dPV \ldots\ldots\ldots(1)$$

$$dH = dU + dPV \ldots\ldots(2)$$

$$dH = dQ$$

$$\therefore \Delta H = \Delta Q = 2256.9 \ KJ$$

$$\Delta U = \Delta H - \Delta(PV)$$

$$= \Delta H - P\Delta V$$

$$P\Delta V = 101.33 \times (1.673 - 0.00104)$$

$$= 169.4 \ kPa \ m^3 = 169.4 \ kNm^{-2}m^3$$

$$= 169.4 \ kJ$$

Then $\qquad \Delta U = 2256.9 - 169.4 \ = 2087.5 \ kJ$

Heat Capacity

Heat is often viewed in relation to its effect on the object to which or from which it is transferred. This is the origin of the idea that a body has a capacity for heat. The smaller the temperature change in a body caused by the transfer of a given quantity of heat, the greater its capacity. Indeed, a heat capacity might be defined:

$$C = \frac{dQ}{dT}$$

The difficulty with this is that it makes C, like Q, a process-dependent quantity rather than a state function. However, it does suggest the possibility that more than one useful heat capacity might be defined. In fact two heat capacities are in common use for homogeneous fluids; although their names belie the fact, both are state functions, defined unambiguously in relation to other state functions.

Heat Capacity at Constant Volume

The constant-volume heat capacity is defined as:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad\qquad 1$$

This definition accommodates both the molar heat capacity and the specific heat capacity (usually called specific heat), depending on whether U is the molar or specific internal energy. Although this definition makes no reference to any process, it relates in an especially simple way to a constant-volume process in a closed system, for which Eq. (1) may be written:

$$dU = C_v dT \qquad\qquad (\text{const V}) \qquad\qquad 2$$

Integration yields:

$$dU = \int_{T_1}^{T_2} C_V \, dT \qquad (\text{const V}) \qquad\qquad 3$$

The combination of this result with $[Q = n\,\Delta U \ (\textbf{\textit{const V}})]$ for a mechanically reversible, constant-volume process gives:

$$Q = n\Delta U = n \int_{T_1}^{T_2} C_V \, dT \qquad \text{(const V)} \qquad\qquad 4$$

If the volume varies during the process but returns at the end of the process to its initial value, the process cannot rightly be called one of constant volume, even though $V_2 = V_1$ and $\Delta V = 0$. However, changes in state functions or properties are independent of path, and are the same for all processes which result in the same change of state. Property changes are therefore calculated from the equations for a truly constant-volume process leading from the same initial to the same final conditions. For such processes Eq. (3) gives $\Delta U = \int C_v dT$, because U, Cv, and T are all state functions or properties. On the other hand, Q does depend on path, and Eq. (4) is a valid expression for Q only for a *constant-volume process*. For the same reason, W is in general zero only for a truly constant-volume process. This discussion illustrates the reason for the careful distinction between state functions and heat and work. The principle that state functions are independent of the process is an important and useful concept.

For the calculation of property changes, an actual process may be replaced by any other process which accomplishes the same change in state.

Such an alternative process may be selected, for example, because of its simplicity.

Heat Capacity at Constant Pressure

The constant-pressure heat capacity is defined as:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad\qquad 5$$

Again, the definition accommodates both molar and specific heat capacities, depending on whether H is the molar or specific enthalpy. This heat capacity relates in an especially simple way to a constant-pressure, closed-system process, for which Eq. (5) is equally well written:

$$dH = C_P dT \qquad \text{(const P)} \qquad\qquad 6$$

Whence

$$\Delta H = \int_{T_1}^{T_2} C_P dT \qquad \text{(const P)} \qquad\qquad 7$$

For a mechanically reversible, constant-pressure process, this result may be combined with $Q = n\,AH\ (const\ P)$ to give

$$Q = n\,AH = n\int_{T_1}^{T_2} CpdT \qquad (const\ P\ )$$

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Since $H,\ C_p,\ and\ T$ are all state functions, Eq. (7) applies to any process for which $P_2 = P_I$ whether or not it is actually carried out at constant pressure. However, only for the mechanically reversible, constant-pressure process can heat and work be calculated by the equations $Q = n\Delta H$, $Q = n\int C_P\,dT$, and $W = -Pn\Delta V$

Example

Air at 1 bar and 298.15 K (25°C) is compressed to 5 bar and 298.15 K (25°C) by two different mechanically reversible prossece:

a) Cooling at constant pressure followed by heating at constant volume.
b) Heating at constant volume followed by cooling at constant pressure.

Calculate the heat and work requirement and ΔU and ΔH of the air of each path.

The following heat capacity for air may be assumed independent of tempreture:

$$C_v = 20.78 \qquad and \qquad C_P 29.10\ \text{J mol}^{-1}\text{K}^{-1}$$

Assume also for air that PV/T is constant, regardless of the changes it undergoes. At 298.15 K (25°C) and 1 bar for molar valume of air is 0.02479 m³ mol⁻¹.

Solution

$$V_2 = V_1\frac{P_1}{P_2} = 0.02479\left(\frac{1}{5}\right) = 0.004958\ m^3$$

a) During the first step the air is cooled at the constant pressure of 1 bar until the final valume of 0.004958 m³ is reached. the temperature of the air at the end of the cooling step is

$$T_2 = T_1\frac{V_2}{V_1} = 298.15\left(\frac{0.004958}{0.02479}\right) = 59.63\ K$$

$$Q = \Delta H = C_P \Delta T = (29.10)(59.63 - 298.15) = -6941J$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P\Delta V$$
$$= -6941 - (1 \times 10^5)(0.004958 - 0.02479) = -4958J$$

During the second step the valume held constant at V_2 while the air is heated to its final state

$$\Delta U = Q = C_V \Delta T = (20.78)(298.18 - 59.63) = 4958J$$

$$Q_{total} = -6941 + 4958 = -1983J$$

$$\Delta U = -4958 + 4958 = 0$$

From first law $\Delta U = Q + W$

$$0 = -1983 + W$$

$$W = 1983J$$

$\Delta H = \Delta U + \Delta(PV)$ also applies to the entire process, but $T_2 = T_1$, and therefore, $P_1 V_1 = P_2 V_2$, Hence $\Delta(PV) = 0$ and

$$\Delta H = \Delta U = 0$$

b) Two different steps are used in this case to reach the same final state of the air. In the first step the air is heated at constant volume equil to its intial value until the final pressure of 5 bar is reached. The air tempreture at the end of this step is:

$$T_2 = T_1 \frac{P_2}{P_1} = 298.15 \left(\frac{5}{1}\right) = 1490.75\ K$$

For this step the volume is constant, and

$$Q = \Delta U = C_V \Delta T = (20.78)(1490.75 - 298.15) = 24788J$$

During the second step the air is cooled at constant pressure of 5 bar to its final state:

$$Q = \Delta H = C_P \Delta T = (29.10)(298.15 - 1490.75) = -34703J$$

Also

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P\Delta V$$

$$\Delta U = -34703 - (5 \times 10^5)(0.004958 - 0.02479) = -24788 J$$

For the two steps combined,

$$Q = 24788 - 34703 = -9915 J$$

$$\Delta U = 24788 - 24788 = 0$$

$$W = \Delta U - Q = 0 - (-9915) = 9915 J$$

As before $\Delta H = \Delta U = 0$

Example 2 Calculate the internal energy and enthalpy changes resulting if air changes from an initial state of 5°C and 10 bar, where its molar volume is 2.312 $\times 10^{-3}$ m³·mol⁻¹, to a final state of 60°C and 1 bar. Assume also that air remains a gas for which PV/T is constant and that CV = 20.785 and CP = 29.100 J·mol⁻¹·K⁻¹.

Solution

Because property changes are independent of process, calculations may be based on any process that accomplishes the change. Here, we choose a two-step, mechanically reversible process wherein 1 mol of air is (a) cooled at constant volume to the final pressure, and (b) heated at constant pressure to the final temperature. Of course, other paths could be chosen, and would yield the same result.

$$T_1 = 5 + 273.15 = 278.15 \text{ K} \qquad T_2 = 60 + 273.15 = 333.15 \text{ K}$$

With $PV = kT$, the ratio T/P is constant for step (a). The intermediate temperature between the two steps is therefore:

$$T' = (278.15)(1/10) = 27.82 \text{ K}$$

and the temperature changes for the two steps are:

$$\Delta T_a = 27.82 - 278.15 = -250.33 \text{ K}$$
$$\Delta T_b = 333.15 - 27.82 = 305.33 \text{ K}$$

For step (a), by Eqs. (2.17) and (2.14),

$$\Delta U_a = C_V \, \Delta T_a = (20.785)(-250.33) = -5203.1 \text{ J}$$
$$\Delta H_a = \Delta U_a + V \, \Delta P_a$$
$$= -5203.1 \text{ J} + 2.312 \times 10^{-3} \text{ m}^3 \times (-9 \times 10^5) \text{ Pa} = -7283.9 \text{ J}$$

For step (b), the final volume of the air is:

$$V_2 = V_1 \frac{P_1 T_2}{P_2 T_1} = 2.312 \times 10^{-3} \left(\frac{10 \times 333.15}{1 \times 278.15} \right) = 2.769 \times 10^{-2} \text{ m}^3$$

By Eqs. (2.21) and (2.14),

$$\Delta H_b = C_P \, \Delta T_b = (29.100)(305.33) = 8885.1 \text{ J}$$
$$\Delta U_b = \Delta H_b - P \, \Delta V_b$$
$$= 8885.1 - (1 \times 10^5)(0.02769 - 0.00231) = 6347.1 \text{ J}$$

For the two steps together,

$$\Delta U = -5203.1 + 6347.1 = 1144.0 \text{ J}$$
$$\Delta H = -7283.9 + 8885.1 = 1601.2 \text{ J}$$

Example 2