Thermodynamics

TOPICS COVERED

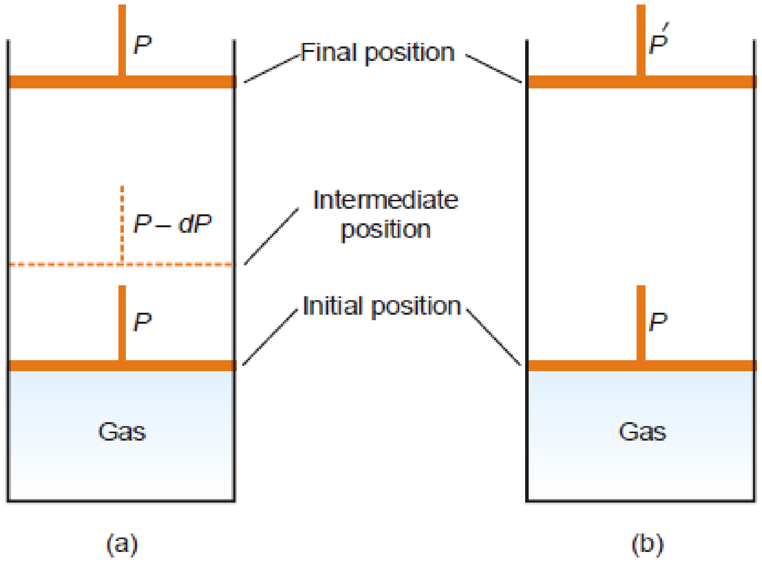
- Reversible and irreversible processes
- Isothermal reversible expansion work of an ideal gas
- Isothermal irreversible expansion work of an ideal gas
- Maximum work done in reversible expansion
- Maximum work done in reversible expansion
- Solved Numericals

REVERSIBLE AND IRREVERSIBLE PROCESSES

- A thermodynamic reverse process is one that takes place infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of the system.
- When a process goes from the initial to the final state in a single step and cannot be carried in the reverse order, it is said to be an irreversible process

(a) Reversible expansion occurs by decreasing the pressure on the piston by infinitesimal amounts.

(b) Irreversible expansion occurs by sudden decrease of pressure from P to P’, when the gas expands rapidly in a single operation.

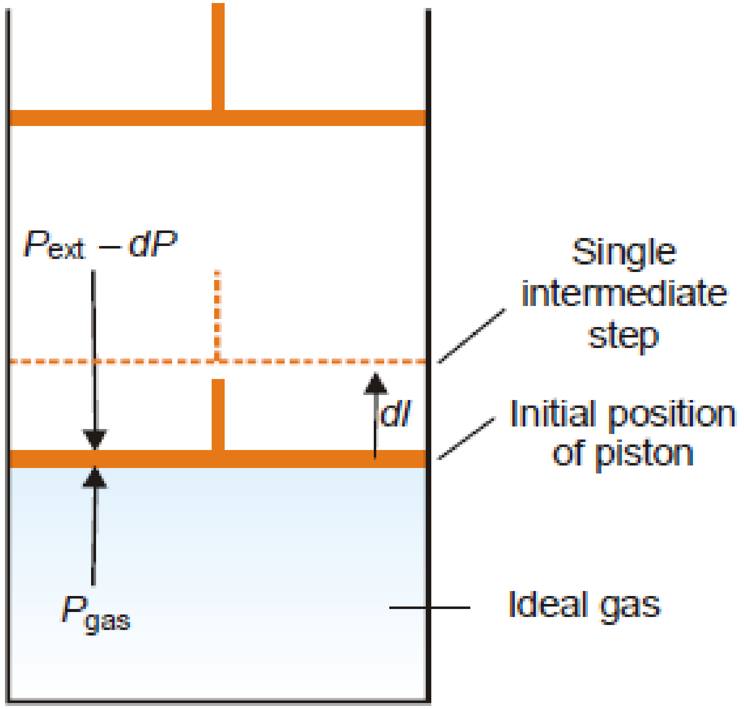


DIFFERENCES BETWEEN REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible Process	Irreversible Process
1. It takes place in infinite number of infinitesimally small steps and it would take *infinite time to occur.*	1. It takes place *infinite time.*
2. It is *imaginary as it assumes the presence* of frictionless and weightless piston.	2. It is *real and can be performed actually.*
3. It is in equilibrium state at *all stages of the* operation.	3. It is in equilibrium state only at the *initial and final stages of the operation.*
4. All changes are *reversed when the process* is carried out in reversible direction.	4. After this type of process has occurred all changes *do not return to the initial* state by themselves.
5. It is extremely slow.	5. It proceeds at *measureable speed.*
6. Work done by a reversible process is *greater than the corresponding* irreversible process.	6. Work done by a irreversible process is *smaller than the corresponding* reversible process.

ISOTHERMAL REVERSIBLE EXPANSION WORK OF AN IDEAL GAS

The reversible expansion of the gas takes place in a finite number of infinitesimally small intermediate steps. To start with the external pressure, P_{ext}, *is arranged equal to the internal* pressure of the gas, P_{gas}, *and the piston remains* stationary. If P_{ext} *is decreased by an infinitesimal* amount *dP the gas expands reversibly and the* piston moves through a distance *dl*.



Since *dP is so small, for all practical* purposes,

Pext = Pgas = P

The work done by the gas in one infinitesimal step *dw, can be expressed as*

dw = P × A × dl (A = cross-sectional area of piston)

= P × dV

where *dV is the increase in volume*

The total amount of work done by the isothermal reversible expansion of the ideal gas from V_1 *to* V_2 *is, therefore,*

$$w = -\int_{v_1}^{v_2} PdV$$

By the ideal gas equation

$$P = \frac{nRT}{V}$$

$$\therefore \quad w = -\int_{v_1}^{v_2} \frac{nRT}{V} dV$$

$$= -nRT \int_{v_1}^{v_2} \frac{dV}{V}$$

which integrates to give

$$w = -nRT \ln \frac{V_2}{v_1}$$

$$P_1V_1 = P_2V_2$$
$$V_2/V_1 = P_1/P_2$$
$$w = -\,nRT\ \ln\frac{P_1}{P_2} = -2.303\ nRT\ \log\frac{P_1}{P_2}$$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with the sign changed. Here the pressure on the piston, Pext, is increased by dP which reduces the volume of the gas.

ISOTHERMAL IRREVERSIBLE EXPANSION WORK OF AN IDEAL GAS

Suppose we have an ideal gas contained in a cylinder with a piston. This time the process of expansion of the gas is performed irreversibly *i.e., by instantaneously dropping the external pressure, P_{ext}, to the final pressure P2. The work done by the system is now against the pressure P2 throughout* the whole expansion and is given by the following expression :

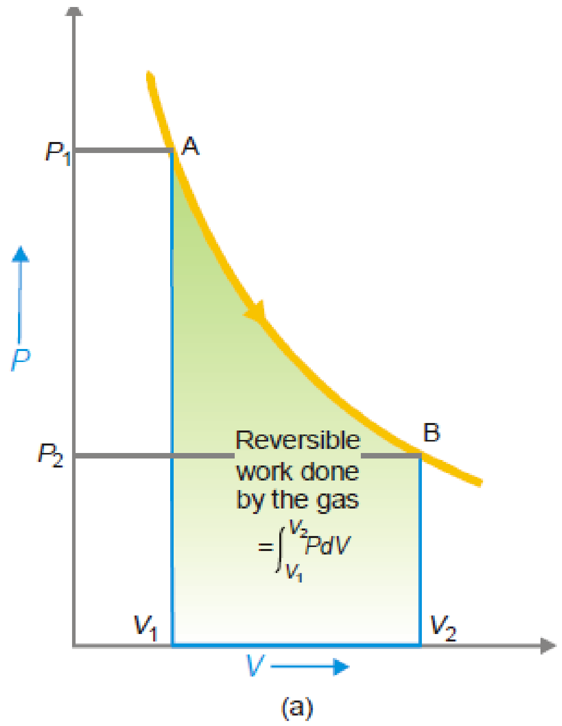
$$w = -P_{ext} \int_{V_1}^{V_2} dV$$

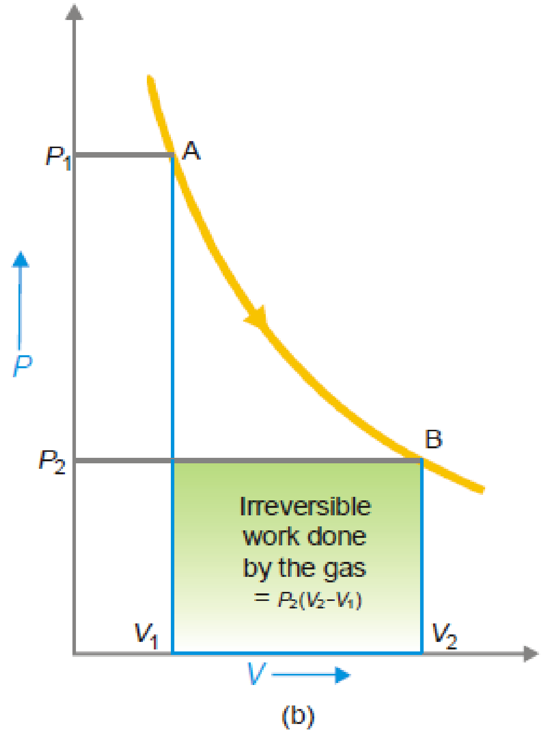
$$= P_2 (V_2 - V_1)$$

$$= P_2\, dV$$

MAXIMUM WORK DONE IN REVERSIBLE EXPANSION

The isothermal expansion of an ideal gas may be carried either by the *reversible process or irreversible process as stated above*





(*a*) The reversible work of expansion; (*b*) The irreversible work done by the gas when the external pressure is at once dropped to the final value P_2.

MAXIMUM WORK DONE IN REVERSIBLE EXPANSION

The reversible expansion is shown in Fig. in which the pressure is falling as the volume increases. The reversible work done by the gas is given by the expression

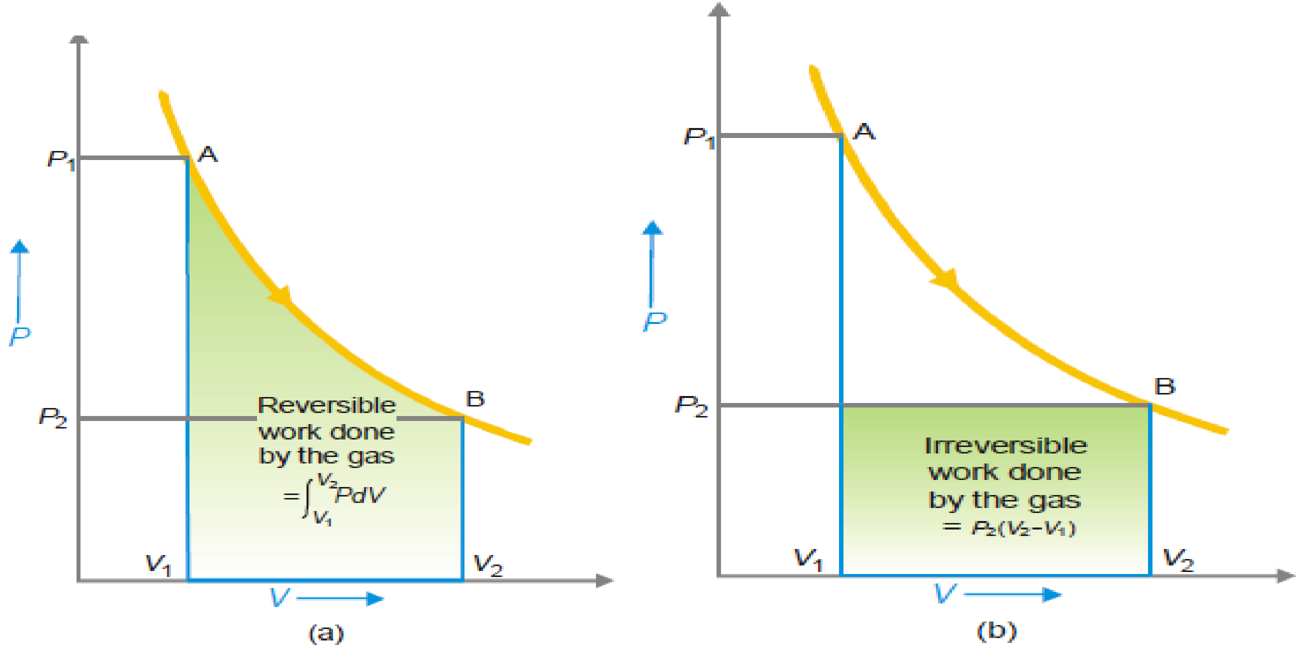
$$-w_{irr} = \int_{v_1}^{v_2} PdV$$

which is represented by the shaded area.

If the expansion is performed irreversibly by suddenly reducing the external pressure to the final pressure *P2, the irreversible work is given by*

$– w_{in} = P2\ (V2 – V1)$

which is shown by the shaded area



MAXIMUM WORK DONE IN REVERSIBLE EXPANSION

Thus mechanical work is not a state function as it depends on the path by which the process is performed rather than on the initial and final states. It is a path function.

The work done in the reversible expansion of a gas is the maximum work that can be done by a system (gas) in expansion between the same initial (A) and final state (B).

work always depends on the external pressure, P_{ext}; *the larger the* P_{ext} *the more* work is done by the gas. But the P_{ext} *on the gas cannot be more than the pressure of the gas,* P_{gas} *or* a compression will take place.

Thus the largest value P_{ext} *can have without a compression taking* place is equal to P_{gas}. *But an expansion that occurs under these conditions is the reversible expansion.*

Thus, maximum work is done in the reversible expansion of a gas.

Solved Numericals

Problem: One mole of an ideal gas at 25 ºC is allowed to expand reversibly at constant temperature from a volume of 10 litres to 20 litres. Calculate the work done by the gas in joules and calories.

SOLUTION

$$w = -\,nRT\ \ln\frac{V_2}{V_1} = -2.303\ nRT\ \log\frac{V_2}{V_1}$$

$$= -2.303 \times 8.314 \times 298 \log\frac{20}{10} = -1717.46\ \text{J}$$

$$= -1717.46\ \text{J} \times \frac{1.987\ \text{cal}}{8.314\ \text{J}} = -\mathbf{410.46\ cal}$$

Problem: Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25ºC.

Solution:

$$w = -\,nRT\ \ln\frac{P_1}{P_2}$$

$$= -1 \times 8.314 \times 298 \times 2.303 \log 5$$

$$= -3988\ \mathrm{J}$$

$$= -\ \mathbf{3.988\ kJ}$$

References

Text Books

1. Atkins, P. W. & Paula, J. de ***Atkin's Physical Chemistry***10th Ed., Oxford University Press (2014).

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THANK YOU