Kinetic Theory of Gases is?

Continued from Oct 9th

❖ **Isothermal Irreversible Expansion or Compression in One Step:**

- For expansion the external pressure must satisfy the expression
- $Pext \leq p_2$, Let $Pext = p_2$ the work involved is
- $w = - Pext\ (\Delta V) = -p_2\ (V_2 - V1)$ (15)
- since $V_2 > V_1$. w = -ve fig 2 displays the magnitude of work as the shaded area.
- For compression the external pressure must satisfy the expression $Pext \leq p_1$, Let $Pext$= p1. The work involved is
- $w = Pext\ (\Delta V) = p_1\ (V_1 - V_2)$ (16)
- since $V_1 > V_2$. w = +ve, fig 3 displays the work as the sha - ded area. Obviously |w_exp | <w_eump (17)
- If $Pext \leq$p2in expansion or $Pext \leq$p1 in compression the desired volume change may be carried out by using set of stops where the movement of piston gets arrested.

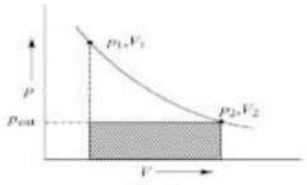


Fig. 2

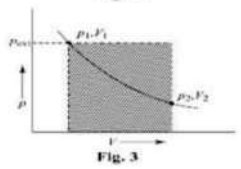


Fig. 3

❖ **Isothermal Irreversible Expansion or Compression in More than One Step:**

- If the above mentioned expa -nsion or compression is carried out in more than one step, the $Pext$ has to be adjusted in each step. Let pext be equal to the final pressure in each step.
- Figure 4 and 5 displays the magnitude of work involved in the expansion and the work involved in compre - ssion carried out in two steps, respectively.

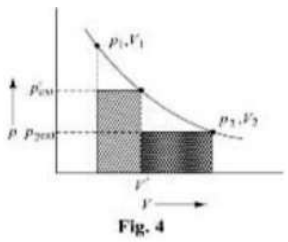
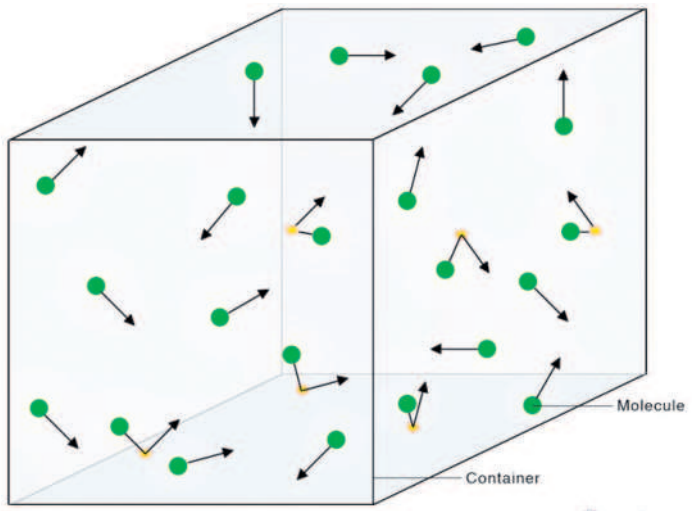


Fig. 4



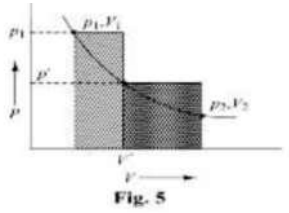


Fig. 5

Notes:

Comparing figs 2 and 4, we find that the magnitude of the work involved has increased in going from one–step to two–step expansion. This trend is continued as the number of steps is increased.

- Comparing figs 3 and 4, we find that the work involved has decreased in going from one–step to two–step compr - ession. This trend is continu -ed as the number of steps is increased.

❖ **Isothermal Reversible Expansion or Compression:**

- In reversible expansion or compression, the external pre -ssure differs infinitesimally from the pressure of gas.

For expansion $Pext = p - dp$

For compression $Pext = p + dp$

The expression of work is

$dw = - Pext\ dV = -(p \mp dp)dV = pdV$

(The product dpdV is ignored as it involves infinite simal quantities)

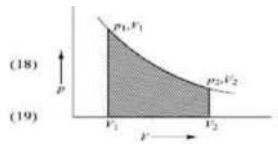
For an ideal gas, $p = nRT/V$.

Hence $dw = -nRT\frac{dv}{V}$ (18)

For a finite change, we have

$$w = -nRT\int_{V_1}^{V_f}\frac{dV}{V} = -nRT\ln\frac{V_f}{V_1} \quad (19)$$

- For expansion $V_1(=V_2) > V_1(=V_1)$, w is negative and the work is done by the system.
- For expansion $V_1(=V_1) > V_1(=V_2)$, w is positive and work is done by on the system.
- Figure displays the magni - tude of work involved in expansion or the work involved in compression is the area under the isotherm.



Note:

- The magnitude of work involved in reversible expan sion is maximum is compa - red to the involved in irreversible expansion.
- The work involved in rever sible compression is minim - um as compared to that in -volved in irreversible comp -ression.

❖ **Adiabatic Irreversible Expansion or Compression:**

- For Adiabatic expansion or compressure, heat is neither enters nor leaves the system. Hence dq=0. The first law of thermodynamics gives
- $dU = dw$ or $nC_{v1m}dT = -Pext\ dV$ or
- $w = -Pext\ (V_2 - V_1) - nCv(T_2 - T_1)$ (20)
- for expansion $V_2 > V_1$, w = < 0, hence $T_1 > T_2$. Thus cool ing is observed during expansion.
- For compression $V_2 < V_1$, w = > 0, and hence $T_1 < T_2$. Thus heating is observed during compression.

❖ **Adiabatic Reversible Expansion or Compression:**

- The involved under rever - sible conditions can be calcul -ated from the expression
- $w = \Delta U - nC_{v1m}(T_2 - T_1)$ (21)
- If the final temperature T2 is not available, it can be evaluated by the expressions derived in the following. For the reversible conditions, $Pext = p \pm dp$ thus we have

$dU = dw$ or $nC_{v1m}dT = Pext dV$

or $nC_{v1m}dT = (p \pm dp)\ dV = pdV$

Replacing p nRT/V; we get

$nC_{v1m}dT = -\left(\frac{nRT}{V}\right)dV$ or

$C_{v1m}\frac{dT}{T} = -R\frac{dV}{V}$

for a finite change we have

$$C_{v1m}\int_{T_1}^{T_2}\frac{dT}{T} = -R\int_{V_1}^{V_2}\frac{dV}{V} \quad \text{or}$$

$C_{v1m}\ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1}$ or

$In\left(\frac{T_2}{T_1}\right)^{C_{v1m}/R} = \ln\left(\frac{V_2}{V_1}\right)$ or

$\left(\frac{T_2}{T_1}\right)^{C_{v1m}/R} = \frac{V_2}{V_1}$ or

$T_2^{C_{v1m}/R}V_2 = T_1^{C_{v1m}/R}V_1$ or

$T^{C_{v1m}/R}V_2$ is constant (2

Since $\frac{C_{v1m}}{R} = \frac{C_{v1m}}{C_{p1m} - C_{v1m}} = \frac{1}{(C_{p1m}/C_{v1m}) - 1} = \frac{1}{\gamma - 1}$

We write the above expression as

- $TV(\gamma^{-1})\ V$ = constant or
- $TV(\gamma^{-1})$ = constant (23)
- In terms of pressure, we have

$T\left(\frac{RT}{T}\right)^{\gamma-1}$ = constant or

$T^{\gamma}p^{1-\gamma}$ = constant (24)

The relation between p and V is

$\left(\frac{pV}{R}\right)V^{\gamma-1}$ = constant or

pV^{γ} = constant (25)

- Equation (23) (25) hold good for an ideal gas undergoing adiabatic reversible expan - sion or compression.

❖ **Expansion Against Vacuum :**

- When the gas undergoes expansion (isothermal or adiabatic) against vacuum. $pext = 0$ Hence the work involved is

$dw = - Pext\ dV = 0$ or $w = 0$

For such an expansion

$\Delta V = 0, \Delta H = 0$ and $\Delta q = 0$ (26)

❖ Molecules	Translational	Rotational	vibrational	Total	C_{v_1m}	C_{v_1m}	Y-C_{v1m}/C_{v1m}
Diatomic	$\frac{3}{2}RT$	$2 \times \frac{1}{2}RT$	RT	$\frac{7}{2}RT$	$\frac{7}{2}R$	$\frac{9}{7}R$	$\frac{9}{7} - 1.286$
Triatomic Linear	$\frac{3}{2}RT$	$2 \times \frac{1}{2}RT$	4RT	$\frac{13}{2}RT$	$\frac{13}{2}R$	$\frac{15}{2}R$	$\frac{15}{2} - 1.153$
nonlinear	$\frac{3}{2}RT$	$2 \times \frac{1}{2}RT$	3RT	6RT	6RT	7RT	$\frac{7}{6} - 1.167$

❖ **Heat Capacities of Gases:**

- The absorption of heat by gases causes an increase in (i) kinetic (or translation) ene - rgy, (ii) rotational energy, and

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Hence, $C_v = \left(\frac{\partial E_k}{\partial T}\right)_v = \frac{3}{2}nR$ and

$C_{v1m} = \frac{3}{2}R$ (27)

Monoatomic gaseous molecules have only translational motion and thus

$C_{v1m} = \frac{3}{2}R$; $C_{v1m} = \frac{3}{2}R + R = \frac{5}{2}R$;

$\gamma = \frac{C_{pm}}{C_{vm}} = \frac{5}{3} = 1.667$ (28)

(iii) vibration energy of gaseous molecules.

- The kinetic energy as given by kinetic theory of gases is Ek = 3/2 nRT
- Diatomic and polyatomic gaseous molecules. Besides having translation motions, also have rotational and vibrational motions.
- Linear and nonlinear molecules have two and three independent rotational mot ions respectively, and each contribute (1/2) NT towards molar energy of the molecule.
- Linear and nonlinear molecules have 3N 5 and 3N 6 independent vibrational motions, respectively, where N is the number of atoms in the molecule. Each vibrat - ional motion contributes RT towards molar energy of the molecule.
- The following is the summ - ary of molar energy contri -butes by each motion towards the total molar energy of the molecules. It also includes, their heat capacities and the ratio of heat capacities.
- **Comment :** The contribution of vibrational motion towards heat capacity is effective only at higher temperatures (which depends on the nature of gas) and thus at ordinary tempera -ture there is contributions from translation and rotatio - nal motions. This gives lower values of C_Vw.

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