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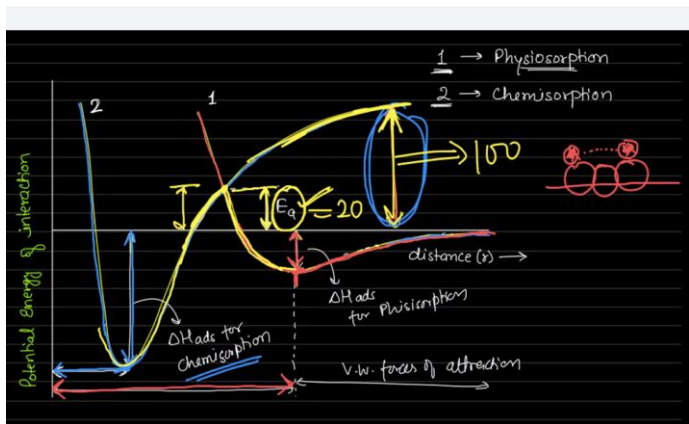
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- Buddha

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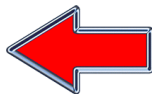
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Comparing ΔE and ΔH

Knowing the enthalpy change of a system tells us a lot about its energy change as well.

✓ Reactions that do not involve gases.

$$\Delta H = \Delta U + \Delta(PV)$$
$$= \Delta U + \Delta n_g RT$$

$$2KOH(aq) + H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + 2H_2O(l)$$

$$\Delta H \approx \Delta U$$
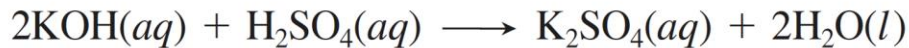
$$\Delta n_g = 0$$

✓ Reactions in which the amount (mol) of gas does not change.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$
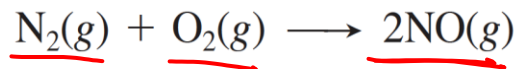
$$\Delta n_g = 2 - 2 = 0 \implies \Delta H = \Delta U$$

✓ Reactions in which the amount (mol) of gas does change.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

$$3 \qquad\qquad 2$$
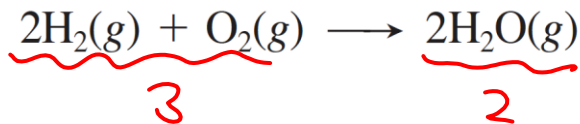
$$\Delta n_g = 2 - 3 = -1$$

$$\Delta H = \Delta U - RT$$

Example

a) $H_2(g) + Cl_2(g) \rightarrow 2HCl\ (g)$; $\Delta H = \Delta U$ bcoz $\Delta n_g = 0$

b) $PCl_5(g) \rightarrow PCl_3\ (g) + Cl_2\ (g)$; $\Delta H = \Delta U + RT$

c) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2\ (g)$; $\Delta H = \Delta U - \frac{1}{2}RT$

Example The difference between heats of reaction at constant pressure and constant volume for the reaction :

$2 C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$ at 25°C in kJ is

ΔH

ΔU
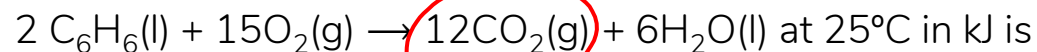
(a) −7.43

(b) +3.72

(c) −3.72

(d) +7.43

$\Delta n_g = -3$

$\Delta H - \Delta U = ?$

$\Delta H = \Delta U + \Delta n_g RT$

$= \Delta U - 3RT$

$\Delta H - \Delta U = -3RT$

$= -3 \times 8.314 \times 298 \ J$

One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0L, 95(K) → (4.0 atm, 5.0 L, 245K) with a change in internal energy, ΔU = 30.0 Latm. The change in enthalpy (ΔH) of the process in L atm is

IIT 2002

(a) 40.0

(b) 42.3

(c) 44.0

(d) not defined, because pressure is not constant

$\Delta U = 30 \text{ L atm}$

$\Delta H = ?$

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

$$\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$$

$$= 30 \text{ L atm} + (20 - 6) \text{ L atm}$$

$$= 44 \text{ L atm}$$

Example Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is

IIT 2004

(a) 11.4 kJ (b) −11.4 kJ   (c) 0 kJ   (d) 4.8 kJ

Isothermal, $\Delta U = 0$

$$= q + w$$

$$q = +2.303\, n R T$$ $q = -W$

$$= +2.303 \times 2 \times 8.314 \times 300$$
$$\overline{\qquad\qquad\qquad 1000 \qquad} \longrightarrow \quad kJ$$

$$= \oplus$$

How do we know the heat of an acid-base reaction or the Calories in a teaspoon of sugar?

Constant-Pressure Calorimetry: For processes that take place at constant pressure, the heat transferred (q_P) is often measured in a coffee-cup calorimeter

Stirrer
Thermometer
Cork stopper
Nested Styrofoam cups (insulation)
Water (surroundings)
Sample (system)

$$m \, c \, \Delta T_{sam}$$

$$\boxed{} = m \, c \, \Delta T$$

Sample

$$\boxed{T_1} = 80\,°C$$

heat lost by sample = heat gained by Calorimeter
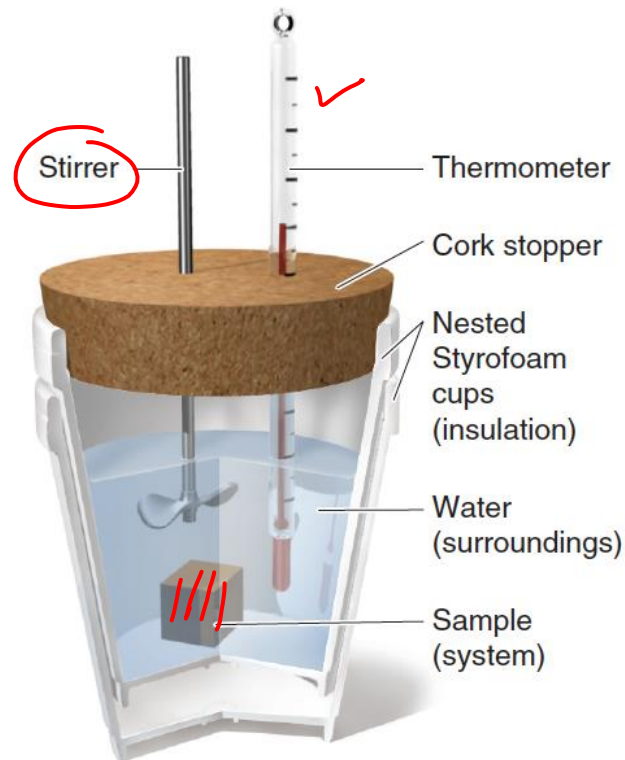
Constant-volume calorimetry is carried out in a bomb calorimeter, a device commonly used to measure the heat of combustion reactions, such as for fuels and foods.

$$\Delta U = q + w = q - P\Delta V$$

$$V = const$$

$$\boxed{\Delta U = q_v}$$

heat lost by bomb $=$ heat gained by calorimeter

$$= mc\Delta T$$

Motorized stirrer

Electrical source
$-\ |\ +$

Thermometer

H_2O-filled container

Ignition wire

System (combustible sample and compressed O_2)

O_2-filled bomb

O_2

Outer covered jacket

Ignition coil

Heat being transferred
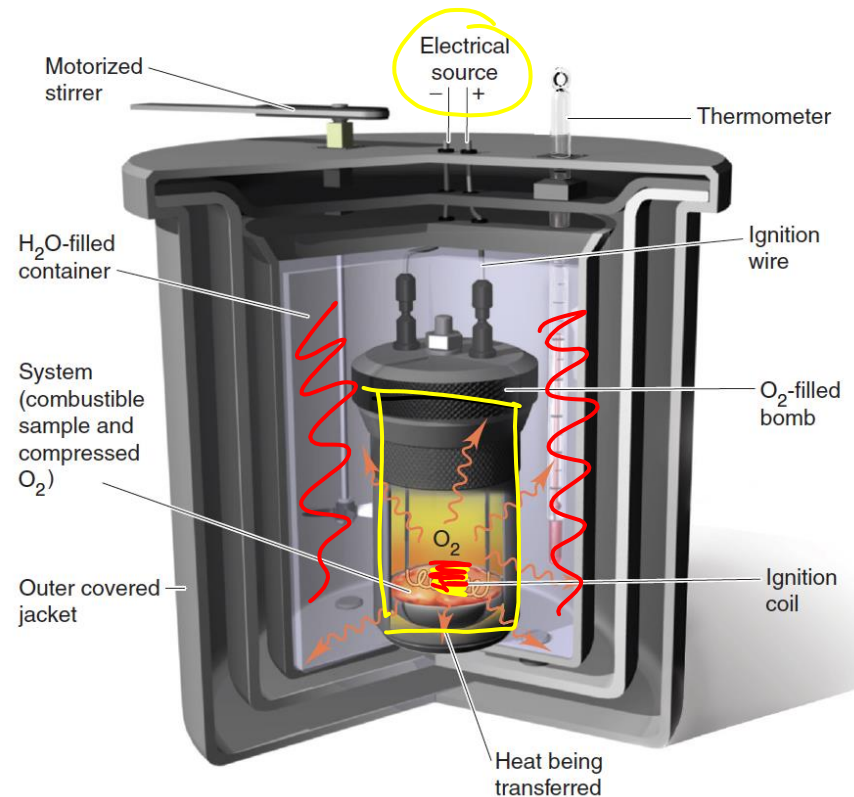
1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation.

C (graphite) + O_2 (g) → CO_2 (g)
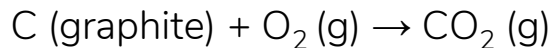
During the reaction, temperature rises from 298 k to 299 k. If the heat capacity of the bomb calorimeter is 20.7kJ/K. What is the enthalpy change for the above reaction at 298 K and 1 atm?

HW
NCERT

For the reaction $FeCO_3$ (s) $\xrightarrow{\Delta}$ FeO(s) + CO_2(g) ; ΔH = 80 KJ at 25^0C

What is ΔU at 25^0 C ?

HW

$$\Delta H = \Delta U + \Delta n_g RT$$
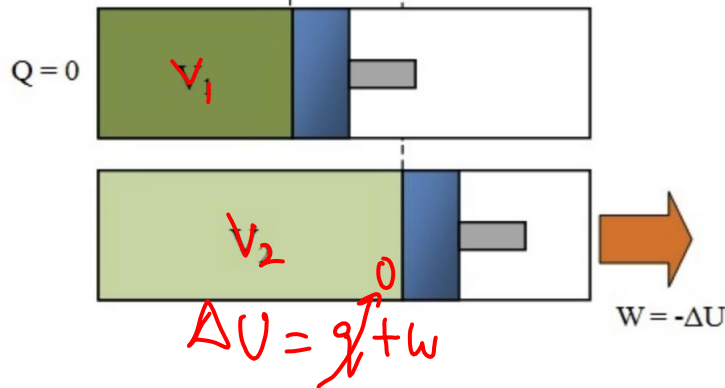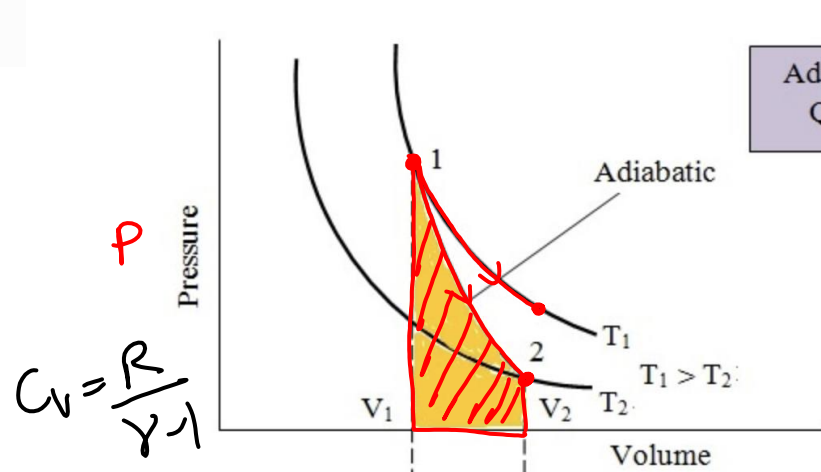
Adiabatic
Q = 0

$\Delta U = W$

$n C_V \, dT = -P_{ext} \, dV$

$\left[PV = nRT \right.$

$n C_V \, dT = -\dfrac{nRT}{V} \, dV$

$\displaystyle \int_{T_1}^{T_2} C_V \dfrac{dT}{T} = \int_{V_1}^{V_2} -\dfrac{R}{V} \, dV$

$\displaystyle \int_{T_1}^{T_2} \dfrac{dT}{T} = (1-\gamma) \int_{V_1}^{V_2} \dfrac{dV}{V}$

$\ln\left(\dfrac{T_2}{T_1}\right) = (1-\gamma) \ln\left(\dfrac{V_2}{V_1}\right)$

P

$C_V = \dfrac{R}{\gamma - 1}$

1

Adiabatic

T_1

2

$T_1 > T_2$

V_1 V_2 T_2

Volume

Q = 0 V_1

V_2 $\Delta U = \cancel{q}^{\,0} + w$

$W = -\Delta U$

Derive $PV^\gamma = $ const. from $TV^{\gamma-1} = $ constant

$$\ln\left(\frac{T_2}{T_1}\right) = (1-\gamma)\ln\left(\frac{V_2}{V_1}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{1-\gamma}$$

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

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

$$\boxed{TV^{\gamma-1} = \text{const}}$$

$$PV^\gamma = \text{const}$$

Ideal gas equ

$$PV = RT$$

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

$$\left(\frac{P_2 V_2}{P_1 V_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$P_2 V_2 V_2^{\gamma-1} = P_1 V_1 V_1^{\gamma-1}$$

valid only for reversible adiabatic

$$T^\gamma P^{1-\gamma} = \text{const}$$

Reversible Adiabatic:

$$\rightarrow \Delta U = \cancel{q}^{0} + W \qquad , \quad \text{we know } PV^{\gamma} = K \qquad P_1 V_1^{\gamma} = P_2 V_2^{\gamma} = K$$

$$\Delta U = -W$$

for rev Process, $P_{ext} \approx P_{Gas}$

$$P = \frac{K}{V^{\gamma}}$$

$$W = \int_{V_1}^{V_2} -P\,dV$$

$$W = -\int_{V_1}^{V_2} \frac{K\,dV}{V^{\gamma}} = -K\int_{V_1}^{V_2} V^{-\gamma}\,dV = \frac{-K\left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right]}{1-\gamma}$$

$$= \frac{-P_2 V_2^{\gamma} \cdot V_2^{1-\gamma} + P_1 V_1^{\gamma} \cdot V_1^{1-\gamma}}{1-\gamma}$$

$$\boxed{W_{Rev.} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}} \quad \Longleftarrow$$

Irreversible Adiabatic:

$$W = -P_{ext} \Delta V$$

since $\Delta U = W$

$$n C_v \Delta T = W$$

$$W_{IRR} = n C_v \Delta T$$

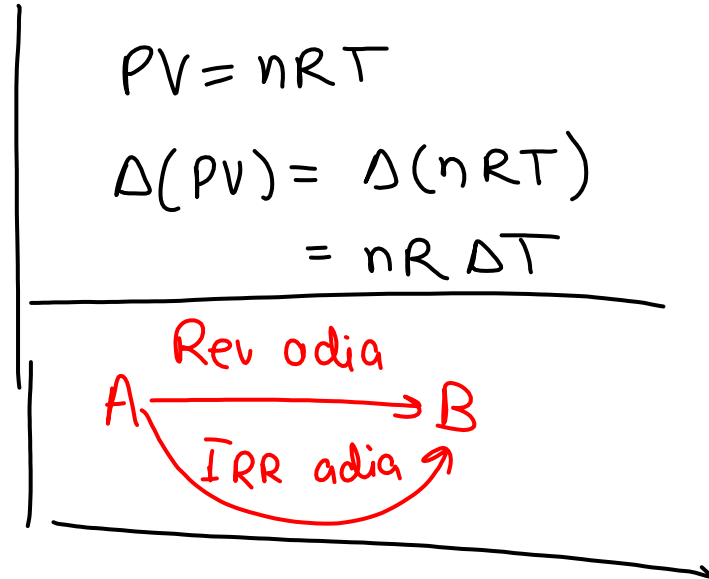$$A \xrightarrow[\text{adia}]{\text{Rev.}} B = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{nR \Delta T}{\gamma - 1} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

$$A \xrightarrow[\text{adia}]{\text{IRR}} C$$

$$PV = nRT$$

$$\Delta(PV) = \Delta(nRT)$$

$$= nR \Delta T$$

$$A \xrightarrow{\text{Rev odia}} B$$

$$\text{IRR adia}$$

What is the final temperature of 0.10 mol mono-atomic ideal gas that performs 75 cal. Of work adiabatically if the initial temperature is 227^0C.

a) 250 K
b) 350 K
c) 150 K
d) 275 K

For a reversible adiabatic ideal gas expansion $\frac{dP}{P}$ is equal to

a) $\gamma \cdot \frac{dV}{V}$

b) $-\gamma \cdot \frac{dV}{V}$

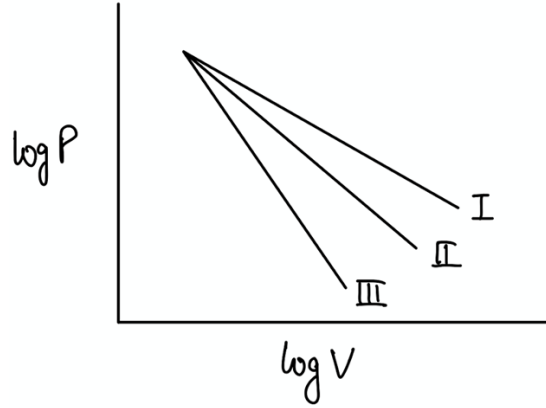c) $\left(\frac{\gamma}{\gamma-1}\right) \cdot \frac{dV}{V}$

d) $\frac{dV}{V}$

The following curves represent adiabatic expansions of gases He, O_2 and CO_2. Which curve represents He?

An ideal gas in a thermally insulated vessel at internal pressure = p_1, volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the below diagram. The nal internal pressure, volume and absolute temperature of the gas are p_2, V_2 and T_2, respectively. For this expansion,
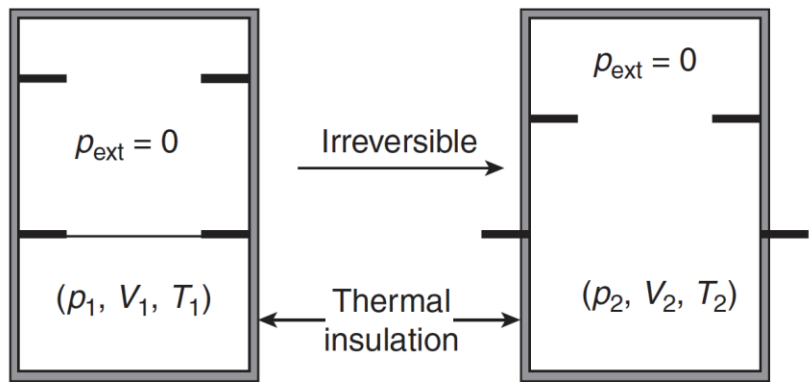
(a) $q = 0$
(b) $T_2 = T_1$
(c) $p_2 V_2 = p_1 V_1$
(d) $p_2 V_2^{\gamma} = p_1 V_1^{\gamma}$

(JEE Advanced 2014)

During an adiabatic process, the pressure of gas is found to be proportional to the cube of the absolute temperature. The ratio of C_P/C_V for the gas is
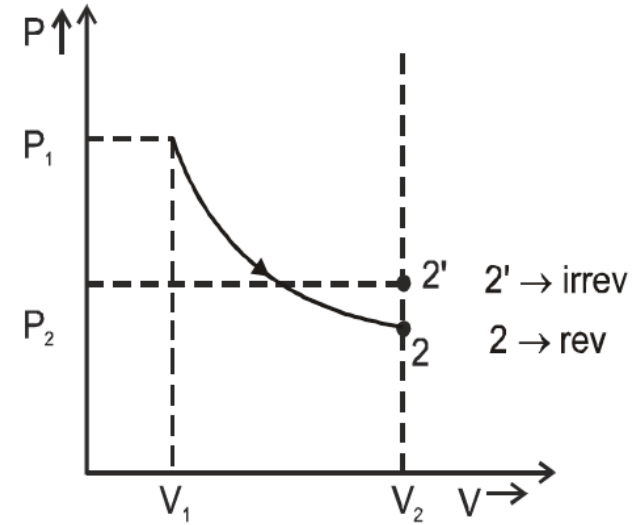
$$\frac{3}{2}$$

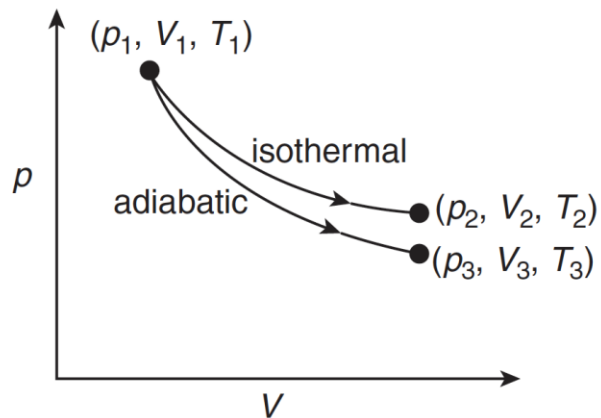$$\frac{5}{3}$$

$$\frac{7}{2}$$

$$\frac{4}{3}$$

Comparison of **Adiabatic** Expansion

The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the below gure. Which of the following statement(s) is (are) correct?

(a) $T_1 = T_2$

(b) $T_3 > T_1$

(c) $W_{isothermal} > W_{adiabatic}$

(d) $\Delta U_{isothermal} > \Delta U_{adiabatic}$

(IIT-JEE 2012)

A liquid of volume of 100L and at the external pressure of 10 atm. The liquid is confined inside an adiabatic bath. External pressure of the liquid is suddenly increased to 100 atm and the liquid gets compressed by 1 L against this pressure then find,

a) Work
b) ΔU
c) ΔH

Two separate experiments were carried out involving adiabatic reversible expansion, taking monoatomic gas in one case and a diatomic gas in the second case. In each case, the initial temperature was T_i and expansion was from volume V_1 to volume V_2. The nal temperatures attained were T_M for monoatomic gas and TD for diatomic gas. Then

a) $T_M = T_D < T_i$
b) $T_M < T_D < T_i$
c) $T_D > T_M > T_i$
d) $T, < T_M < T_f$

Which of the following statements is not correct?

(a) Final temperature in reversible adiabatic expansion is greater than that in irreversible adiabatic expansion.

(b) When heat is supplied to an ideal gas in isothermal process, kinetic energy of gas remains constant.

(c) When an ideal gas is subjected to adiabatic expansion, it gets cooled.

(d) Entropy increases when an ideal gas expands isothermally.

Screen 1 (6:37)

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