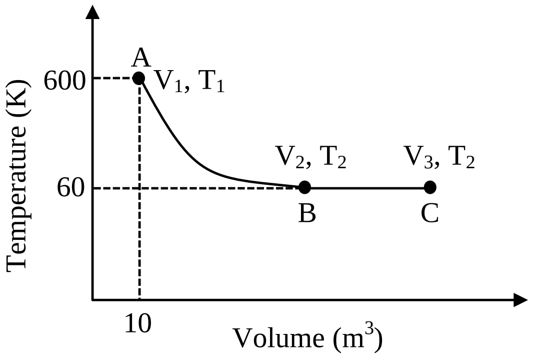
PHYSICAL CHEMISTRY

THERMODYNAMICS-I

1. One mole of an ideal monoatomic gas undergoes two reversible processes ($A \rightarrow B$ and $B \rightarrow C$) as shown in the given figure :



$A \rightarrow B$ is an adiabatic process. If the total heat absorbed in the entire process ($A \rightarrow B$ and $B \rightarrow C$) is $RT_2 \ln 10$, the value of $2 \log V_3$ is _________. **[JEE(Advanced) 2023]**

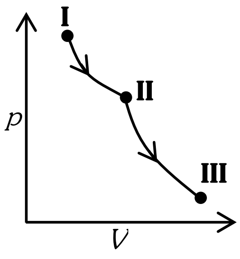
[Use, molar heat capacity of the gas at constant pressure, $C_{p,m} = \frac{5}{2}R$]

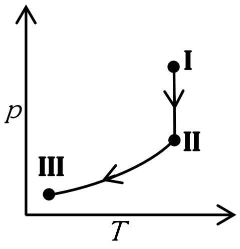
2. 2 mol of Hg(g) is combusted in a fixed volume bomb calorimeter with excess of O_2 at 298 K and 1 atm into HgO(s). During the reaction, temperature increases from 298.0 K to 312.8 K. If heat capacity of the bomb calorimeter and enthalpy of formation of Hg(g) are 20.00 kJ K^{-1} and 61.32 kJ mol^{-1} at 298 K, respectively, the calculated standard molar enthalpy of formation of HgO(s) at 298 K is X kJ mol^{-1}. The value of |X| is ______.

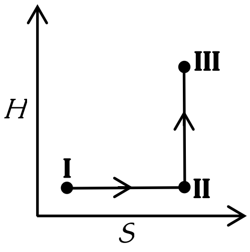
[Given : Gas constant R = 8.3 J K^{-1} mol^{-1}] **[JEE(Advanced) 2022]**

3. An ideal gas undergoes a reversible isothermal expansion from state **I** to state **II** followed by a reversible adiabatic expansion from state **II** to state **III**. The correct plot(s) representing the changes from state **I** to state **III** is(are)

(p : pressure, V : volume, T : temperature, H : enthalpy, S : entropy) **[JEE(Advanced) 2021]**

(A)


(B)


(C)


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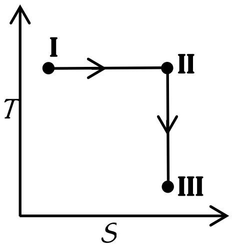
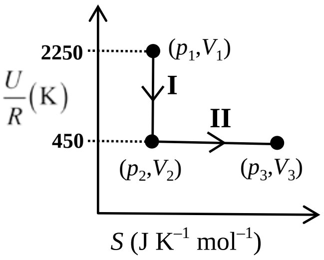


4. One mole of an ideal gas at 900 K, undergoes two reversible processes, **I** followed by **II**, as shown below. If the work done by the gas in the two processes are same, the value of $\ln \frac{V_3}{V_2}$ is ___.

[JEE(Advanced) 2021]



(U: internal energy, S: entropy, p: pressure, V: volume, R: gas constant)

(Given: molar heat capacity at constant volume, $C_{V,\text{m}}$ of the gas is $\frac{5}{2}R$)

5. In thermodynamics the P-V work done is given by

$$w = -\int dV\, P_{\text{ext}}\ .$$

For a system undergoing a particular process, the work done is ,

$$w = -\int dV \left(\frac{RT}{V-b} - \frac{a}{V^2} \right).$$

This equation is applicable to a **[JEE(Advanced) 2020]**

(A) System that satisfies the van der Waals equation of state.

(B) Process that is reversible and isothermal.

(C) Process that is reversible and adiabatic.

(D) Process that is irreversible and at constant pressure.

6. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place.

At 298 K : $\Delta_f H°(SnO_2(s)) = -581.0$ kJ mol^{-1}, $\Delta_f H°(CO_2(g)) = -394.0$ kJ mol^{-1}

$S°(SnO_2(s)) = 56.0$ J K^{-1} mol^{-1}, $S°(Sn(s)) = 52.0$ J K^{-1} mol^{-1} ,

$S°(C\ (s)) = 6.0$ J K^{-1} mol^{-1} , $S°(CO_2(g)) = 210.0$ J K^{-1} mol^{-1}.

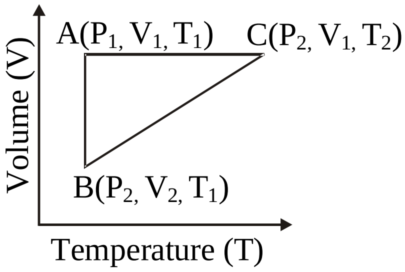
Assume that the enthalpies and the entropies are temperature independent. **[JEE(Advanced) 2020]**

7. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. **[JEE(Advanced) 2019]**

(A) $\frac{3}{2}O_2(g) \rightarrow O_3(g)$ (B) $\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$

(C) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ (D) $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$

8. A reversible cyclic process for an ideal gas is shown below. Here, P , V and T are pressure , volume and temperature , respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively. **[JEE(Advanced) 2018]**



The correct option(s) is (are)

(A) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$ (B) $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

(C) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$ (D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

9. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below :

$2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$

p_{H2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H2})$ is ______.

(Given : total pressure = 1 bar, R (universal gas constant) = 8 $JK^{-1}mol^{-1}$, ln(10) = 2.3. Cu(s) and $Cu_2O(s)$ are mutually immiscible.

At 1250 K : $2Cu(s) + 1/2O_2(g) \rightarrow Cu_2O(s)$; $\Delta G^\theta = -78,000$ J mol^{-1}

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$; $\Delta G^\theta = -1,78,000$ J mol^{-1}; G is the Gibbs energy) **[JEE(Advanced) 2018]**

10. An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is(are) **[JEE(Advanced) 2017]**

(A) The work done on the gas is maximum when it is compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1

(B) The work done on the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.

(C) The change in internal energy of the gas (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$

(D) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.

11. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are

$$\Delta_f G° [C(graphite)] = 0 \text{ kJ mol}^{-1}$$

$$\Delta_f G° [C(diamond)] = 2.9 \text{ kJ mol}^{-1}$$

The standard state means that the pressure should be 1 bar , and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2×10^{-6} m^3 mol^{-1}. If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is **[JEE(Advanced) 2017]**

[Useful information : 1 J = 1 kg m^2 s^{-2} ; 1 Pa = 1 kg m^{-1} s^{-2} ; 1 bar = 10^5 Pa]

(A) 14501 bar (B) 29001 bar (C) 58001 bar (D) 1405 bar

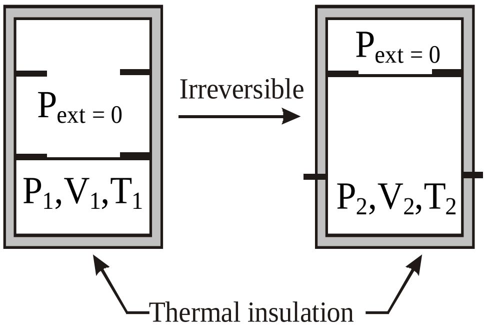
12. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in J K^{-1} is - **[JEE(Advanced) 2016]**

(1 L atm = 101.3 J)

(A) 5.763 (B) 1.013 (C) –1.013 (D) –5.763

13. An ideal gas in thermally insulated vessel at internal pressure = P_1, volume = V_1 and absolute temperature = T_1 expands irrversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2, V_2 and T_2, respectively. For this expansion,

[JEE(Advanced) 2014]



(A) q = 0 (B) $T_2 = T_1$ (C) $P_2V_2 = P_1V_1$ (D) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

SOLUTIONS

1. Ans. (7)

Sol. For A → B $\quad 600\,V_1^{\gamma-1} = 60V_2^{\gamma-1}$ ($\gamma = 5/3$)

(Reversible adiabatic)

$\Rightarrow$ $600\,(V_1)^{2/3} = 60\,(V_2)^{2/3}$

$\Rightarrow$ $10 = \left(\frac{V_2}{V_1}\right)^{2/3}$

$\Rightarrow$ $10 = \left(\frac{V_2}{10}\right)^{2/3}$

$\Rightarrow$ $V_2 = 10(10)^{3/2} = 10^{5/2}$

Now, $q_{net} = RT_2\,ln\,10 = 60\,R\,ln\,10 = q_{AB} + q_{BC}$

$\because$ $q_{AB} = 0$

$\Rightarrow$ $q_{BC} = 60\,R\,ln\,10 = 60\,R\,ln\,\frac{V_3}{V_2}$ [$\because$ B → C is reversible isothermal]

$\Rightarrow$ $60\,R\,ln\,10 = 60\,R\,ln\left(\frac{V_3}{10^{5/2}}\right)$

$\Rightarrow$ $\log 10 = \log V_3 - \frac{5}{2}$

$\Rightarrow$ $\log V_3 = \frac{7}{2} \Rightarrow 2\log V_3 = 7$

2. Ans. (89.00 - 91.00)

Sol. $Q_{rxn} = C\Delta T$

$|\Delta U| \times 2 = 20 \times 14.8$

$|\Delta U| = 148$ kJ/mol

$\Delta U = -148$ kJ/mol

$Hg(g) + \frac{1}{2}O_2(g) \longrightarrow HgO(s) : \Delta U = -148$ kJ/mol

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

$= -148 - \frac{3}{2} \times \frac{8.3}{1000} \times 298 = -151.7101$

$Hg(l) + \frac{1}{2}O_2(g) \longrightarrow HgO(s)$

$\Delta H = -151.7101 + 61.32 = -90.39$ kJ/mol

3. Ans. (A, B, D)

Sol. From state I to II (Reversible isothermal expansion)

$\Rightarrow$ P decreases, V increases, T constant
H constant & S increases.

From state II to III (Reversible adiabatic expansion)

$\Rightarrow$ P decreases, V increases, T decreases
H decreases, S constant

$\therefore$ Plots (A), (B), (D) are correct while (C) is wrong as from II to III, H is decreasing.

4. Ans. (10)

Sol. $\Delta U_I = nC_{v,m}\,\Delta T = W_I\ \{q_I = 0\}$

$$-1800\,R = 1 \times \frac{5R}{2} \times \Delta T = \Delta T = -720\text{ K}$$

$T_2 = 180$ K

$$W_{II} = W_I = -1800\,R = -1 \times R \times 180 \ln\left(\frac{V_3}{V_2}\right)$$

$$l\text{n}\left(\frac{V_3}{V_2}\right) = 10 \Rightarrow 10$$

5. Ans. (A, B, C)

Sol. For 1 mole Vander Waal's gas

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

If $P_{ext} = P$, means process is reversible. For Vanderwaal gas, expression is correct for all reversible process.

6. Ans. (935.00)

Sol. $SnO_{2(S)} + C_{(S)} \longrightarrow Sn_{(S)} + CO_{2(g)}$

$\Delta H^\circ_{rxn} = [-394] - [-581] = 187$ kJ/mole

$\Delta S^\circ_{rxn} = [52 + 210] - [56 + 6]$

$= 200$ J/k–mole

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{187 \times 1000}{200} = 935\text{K}$$

7. Ans. (A, B)

Sol. Enthalpy of formation is defined as enthalpy change for formation of 1 mole of substance from its elements, present in their natural most stable form.

8. Ans. (B, C)

Sol. AC → Isochoric

AB → Isothermal

BC → Isobaric

$q_{AC} = \Delta U_{BC} = nC_V\,(T_2 - T_1)$

$W_{AB} = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$ A (wrong)

$q_{BC} = \Delta H_{AC} = nC_P\,(T_2 - T_1)$

$W_{BC} = -P_2(V_1 - V_2)$ B (correct)

$nC_P\,(T_1 - T_2) < nC_V(T_1 - T_2)$ C (correct)

$\Delta H_{CA} < \Delta U_{CA}$

D (wrong)

9. Ans. (–14.6)

Sol. $2Cu(s) + \frac{1}{4}O_2(g) \rightarrow 1Cu_2O(s)$ $\quad \Delta G^\circ = -78$ kJ

$[H_2(g) + \frac{1}{2}O_2 \rightarrow H_2O(g)$ $\quad \Delta G^\circ = -178$ kJ$] \times (-1)$

Hence, $2Cu(s) + H_2O(g) \rightarrow Cu_2O + H_2(g)$ $\quad \Delta G^\circ = +100$ kJ

$\Delta G = \Delta G^\circ + RT \ln Q$

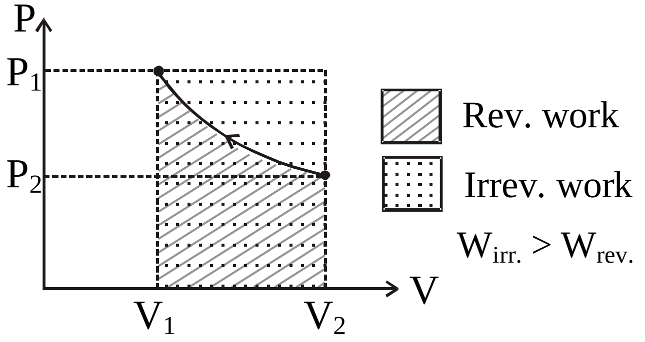
$$0 = +100 + \frac{8}{1000} \times 1250 \ln \frac{p_{H_2}}{p_{H_2O}}$$

$$-\frac{100 \times 1000}{8} = 1250 \ln \frac{p_{H_2}}{\left(\frac{1}{100} \times 1\right)}$$

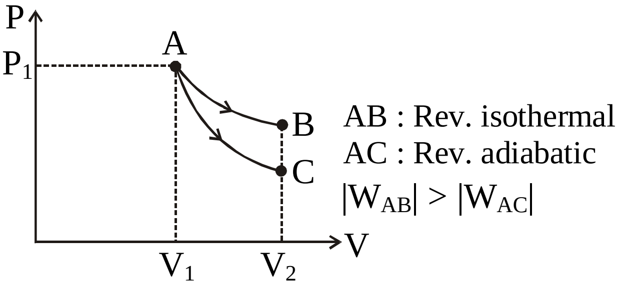
$\ln P_{H_2} = -14.6$

10. Ans. (A, B, D)

Sol. (A)



(B)



(C) (i) $\Delta U = nC_v \Delta T = 0$ (isothermal hence $\Delta T = 0$)

(ii) $\Delta U = q + w = -ve$ ($q = 0$, $w < 0$)

$\Delta U = nC_v \Delta T \Rightarrow \Delta T < 0$

(D) $q = 0$ (adiabatic), $w = 0$ (free expansion)

$\Delta U = 0 \Rightarrow \Delta T = 0$ (isothermal)

11. Ans. (A)

Sol. C(graphite) → C(diamond) ; $\Delta G^0 = \Delta_f G^0{}_{diamond} - \Delta_f G^0{}_{graphite} = 2.9$ kJ/mole at 1 bar

As $dG_T = V.dP$

$$\int_{\Delta G_1}^{\Delta G_2} d(\Delta G_T) = \int_{P_1}^{P_2} \Delta V.dP$$

$\Delta G_2 - \Delta G_1 = \Delta V.\ (P_2 - P_1)$

$(2.9 \times 10^3 - 0) = (-2 \times 10^{-6})\ (1 - P_2)$

$P_2 - 1 = \frac{2.9 \times 10^3}{2 \times 10^{-6}}$ Pa $= 1.45 \times 10^4$ bar

$P_2 = 14501$ bar

12. Ans. (C)

Sol. From 1st law of thermodynamics

$q_{sys} = \Delta U - w = 0 - [-P_{ext}.\Delta V]$

$= 3.0$ atm × (2.0 L – 1.0 L) = 3.0 L-atm

$\therefore\ \Delta S_{surr} = \frac{(q_{rev})_{surr}}{T} = -\frac{q_{sys}}{T} = -\frac{3.0 \times 101.3\,J}{300K} = -1.013$ J/K

13. Ans. (A, B, C)

Sol. Process is adiabatic $q = 0$

$P_{ext} = 0$ $w = 0$

$\Delta U = q + w = 0$

The change in internal energy of an ideal gas depends only on temperature therefore $\Delta T = 0$ hence process is isothermal therefore

$T_2 = T_1$ & $P_2V_2 = P_1V_1$

D is incorrect, it is valid for adiabatic reversible process