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## CHEMISTRY

## BOOKS - MAXIMUM PUBLICATION

## THERMODYNAMICS

## Example

1. Hot coffee in a thermosflask is an example of system.
2. Which of the following statement is incorrect about internal energy? a) The absolute value of internal energy cannot be determined b) The internal
energy of one mole of a substance is same at any temperature or pressure c) The measurement of heat
change during a reaction by bomb calorimeter is
equal to the internal energy change d) Internal
energy is an extensive property
A. The absolute value of internal energy cannot be
determined
B. The internal energy of one mole of a substance is same at any temperature or pressure
C. The measurement of heat change during a reaction by bomb calorimeter is equal to the internal energy change
D. Internal energy is an extensive property

## Answer: B

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3. For which of the following the standard enthalpy is not zero?
A. C (Diamond)

## B. C (Graphite)

C. Liquid mercury
D. Rhombic sulphur

Answer: A

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## 4. Say TRUE or FALSE?

Any spontaneous process must lead to a net increase in entropy of the universe.
5. The $\Delta H$ for a reaction is-30kJ. On the basis of this
fact, we can conclude that the reaction
A. Gives off thermal energy
B. Is fast
C. Is slow
D. Is spontaneous

## Answer: A

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6. Write the type of system in each of the following:
a) Hot water taken in an open vessel
b) Hot water taken in a closed metallic vessel
c) Hot water taken in a thermos flask

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7. In a reversible process the total change in entropy is $\Delta S$ (universe) is

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8. For the reaction $\mathrm{Ag}_{2} \mathrm{O} \rightarrow 2 \mathrm{Ag}+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \Delta S$ and $\Delta$

H are $\quad 6.66 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ and $30.56 \mathrm{kJmol}^{-1}$
respectively. The reaction will not be spontaneous at what temperature
A. 4579 K
B. 4589 K
C. 3589 K
D. 4599 K

## Answer:

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9. One mole of methane undergoes combustion to form $\mathrm{CO}_{2}$ and water at $25^{\circ} \mathrm{C}$. The difference between
$\Delta U \& \Delta H$ will be
10. A gas expands from 11 to 61 against a constant pressure of 1 atm and it absorbs 500 J of heat $\Delta U$ is

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11. Born Haber cycle is to find out

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12. a) Explain enthalpy of fusion.
b) Give illustration of fusion of ice.
13. a) What do you meant by enthalpy of vapourisation?
b) Explain enthalpy of sublimation.

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14. One equivalent of an acid reacts completely with one equivalent of a base in dilute solution.
a) Which type reaction is this?
b) $\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}$

On the basis of above equation, explain enthalpy of neutralisation.

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15. a) What is the different between system and surroundings?
b) There are different types of systems. What are they? Explain.
c) Give example for different types of systems.

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16. a) What is meant by enthalpy?
b) Derive an equation for enthalpy change.
c) What is enthalpy change?
17. a) Find the enthalpy of the reaction,

C (graphite) $+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})$
Given,
i)

C(graphite)
$+\frac{1}{2} O_{2}(g) \rightarrow C O(g), \Delta H=-110.5 \mathrm{kJmol}^{-1}$
ii)

CO(g)
$+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}), \Delta \mathrm{H}=-283.0 \mathrm{kJmol}^{-1}$
b) Melting of ice is a spontaneousnprocess. What are the criteria for spontaneity of a process?
18. Explain the following:
i) Enthalpy of atomization
ii) Enthalpy of solution at infinite dilution

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19. The enthalpy change for the reaction,
$N_{2}(g)+3 H_{2}(g) \rightarrow 2 \mathrm{NH}_{3}(g)$ Is -92.38 kJ at 298 K.
What is $\Delta U$ at 298 K ?

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20. What are the two types of heat capacities? How they are related?

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21. Enthalpy and Entropy changes of two reactions are given below: Find out whether they are spontaneous or not at $27^{\circ} C$. Justify.
a) $\Delta H=26 \mathrm{~kJ} / \mathrm{mole}, \Delta S=8.3 \mathrm{~J} / \mathrm{K} / \mathrm{mole}$
b) $\Delta H=-393.4 \mathrm{~kJ} / \mathrm{mole}, \Delta S=6 \mathrm{~J} / \mathrm{K} / \mathrm{mole}$

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22. a) What is enthalpy of solution?
b) What is enthalpy of dilution?
23. What is the significance of the second law of thermodynamics in the spontaneity of exothermic and endothermic reactions?

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24. Explain the importance of third law of thermodynamics.

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25. $\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}+120_{2} \rightarrow 12 \mathrm{CO}_{2}+11 \mathrm{H}_{2} \mathrm{O}$

Consider this equation and answer the following questions.
a) Thermodnamically, which type reaction is this?
b) What is enthalpy of combustion?
c) Give another example.

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26. Bond dissociation energies of hydrogen and nitrogen are 430 kJ and 941.8 kJ respectively and the enthalpy of formation of $\mathrm{NH}_{3}$ is -46 kJ . What is the bond energy of $\mathrm{N}-\mathrm{H}$ bond?

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27. In 1840, G.H.Hess (a Russian chemist) proposed an important generalisation of thermochemistry which is known after his name as Hess's law.
a) State Hess's law.
b) Give illustration of Hess's law.

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28. $\Delta U=q-p \Delta V$. If the process is carried out at constant volume, then $\Delta V=0$. Answer the following questions.
a) Give the equation for $\Delta U$.
b) 1000 J was supplied to a system at constant volume.

It resulted in the increase of temperature of the system from $45^{\circ} C$ to $50^{\circ} \mathrm{C}$. Calculate the change in internal energy.

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29. Thermodynamics deals with macroscopic properties.
a) What is the difference between extensive and intensive properties?
b) Classify the following properties into extensive and intensive.

Pressure, Mass, Volume, Temperature, Density, Heat
capacity, Viscosity, Surface tension, Internal energy,
Molar heat capacity, Refractive index, Enthalpy, Specific heat capacity.

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30. a) What is meant by state of the system and state
variables?
b) Give any four examples for state variables/state functions.
31. a) Explain the Zeroth law of thermodynamics.
b) What are the important modes of transference of energy. Explain.

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32. a) Explain the symbols and sign conventions of heat and work.
b) Explain internal energy.
33. Fill in the blanks.
a) If heat is released, ' $q$ ' is
b) For exothermic process ' $\Delta H^{\prime}$ ' is
c) If work is done on the system, 'w' is
d) For endothermic process ' $\Delta H$ ' is
e) If work is done by the system, 'w' is

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34.a) What is meant by enthalpy of formation?
b) What is the value of standard enthalpy of formation $\left(\Delta_{f} H^{o}\right)$ of an element?
35. First Law of thermodynamics is the law of conservation of energy.
a) Give the mathematical form of the first law.
b) Write the Gibb's equation.
c) What is the sign for $\Delta G$ for a spontaneous process?

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36. a) Predict the sign of $\Delta S$ for the reaction,
$\mathrm{NH}_{3}(g)+\mathrm{HCI}(g) \rightarrow \mathrm{NH}_{4} \mathrm{CI}(s)$
b) The reaction between gaseous hydrogen and
chlorine is
$\mathrm{H}_{2}(g)+\mathrm{CI}_{2}(g) \rightarrow 2 \mathrm{HCI}(g), \Delta_{r} H=-1840 \mathrm{~kJ}$
i) What is the enthalpy of formation of HCl ?
ii) How much heat will be liberated at 298 K and 1 atm for the formation of 365 g of HCl ?

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37. Derive the Meyer's relationship.

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38. a) In a process 701 J of heat is absorbed by a
system and 394 J of work is done by the system. What
is the change in internal energy for the process?
b) What is free expansion? What is the work done during free expansion of an ideal gas?

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39. a) Name the instrument used for measuring the
$\Delta U$ of a process.
b) What is the value of $\Delta G$ for a reaction at equilibrium?
c) $\Delta H$ and $\Delta S$ of a reaction are 30.56 and 0.666 $\mathrm{kJ} / \mathrm{mol}$ respectively at 1 atm pressure. Calculate the temperature at which the reaction is in equilibrium.
40. Thermodynamic process differ based on the manner in which it is carried out.
a) Distinguish between reversible and irreversible processes.
b) Calculate the amount of work done when 2 moles of a gas expands from a volume of 2 L to 6 L isothermally and irreversibly against a constant external pressure of 1 atm.
41. a) What are thermochemical equations?
b) Give an example for a thermochemical equation.

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42. a) Define lattice enthalpy of an ionic compound.
b) What is Born-Haber cycle?

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43. Predict what happens to entropy in the following
changes:
a) Metal is converted into alloy.
b) Solute crystallizes from solution.
c) Hydrogen molecule dissociates.

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44. a) Give the relation between change in enthalpy and change in free energy.
b) Name the above relation.
c) What is the significance of the above relation?

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45. a) Predict in each of the following whether entropy increses or decreases.
i) Sublimation of camphor
ii) $4 \mathrm{Fe}(\mathrm{s})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~g})$
b) The equilibrium constant for a reaction at $30^{\circ} \mathrm{C}$ is
$2.5 \times 10^{-29}$. What will be the value of $\Delta G^{\circ} ?$

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46. a) Explain the effect of temperature on the spontaneity of a process based on Gibbs equation.
b) For a reaction $2 A(g)+B(g) \rightarrow 2 D(g)$, enthalpy and entropy changes are $-20.5 \mathrm{kJmol}^{-1}$ and
$-50.4 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ respectively. Predict whether the reaction occurs at $25^{\circ} \mathrm{C}$.
47. a) Explain the first, second and third laws of thermodynamics.
b) What do you meant by entropy?
c) Explain the spontaneous process.

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48. $U_{1}, \mathrm{q}, \mathrm{w}, U_{2}$ are given. $U_{1}$ is internal energy, q is absorbed heat, w is work done and $U_{2}$ is final energy.
a) Derive an equation for $\Delta U$.
b) Give the equation for w.
c) Calculate the change in internal energy of a system
which absorbs 200 J of heat and 315 J of work is done by the system.

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49. a) Predict whether entropy increases or decreases in the following changes:
i) $l_{2}(S) \rightarrow l_{2}(g)$
ii) Temperature of a crystalline solid is raised from 0 K and 115 K .
iii) Freezing of water
b) Calculate the enthalpy of combustion of methane.

Given that standard enthalpies of formation of
$\mathrm{CH}_{4}, \mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ are $-75.2,-394$ and -285.6 $\mathrm{kJ} / \mathrm{mol}$ respectively.

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50. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

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51. The reaction of cyanamide, $\mathrm{NH}_{2} \mathrm{CN}(s)$ with oxygen was carried out in a bomb calorimeter and $\Delta U$ was found to be $-742.7 \mathrm{kJmol}^{-1}$ at 298 K .

Calculate the enthalpy change for the reaction at 298
K.

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52. Calculate the number of kJ of heat necessary to
raise the temperature of 60 g of aluminium from $35^{\circ} \mathrm{C}$ to $55^{\circ} \mathrm{C}$. Molar heat capacity of Al is 24 J $\mathrm{mol}^{-1} K^{-1}$.

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53. The enthalpy of formation of $\mathrm{CO}(\mathrm{g})$,
$\mathrm{CO}_{2}(g), \mathrm{N}_{2} \mathrm{O}(g), \mathrm{N}_{2} \mathrm{O}_{4}(g)$ are -110, -393, 81 and 9.7 kJ
$\mathrm{mol}^{-1}$ respectively. $\mathrm{N}_{2} \mathrm{O}_{4}+3 \mathrm{CO}(\mathrm{g}) \quad \rightarrow \mathrm{N}_{2} \mathrm{O}(\mathrm{g})+3 \mathrm{CO}_{2}$
(g). Find the value of $\Delta r H$ for the reaction:
A. $666.6 \mathrm{~kJ} \mathrm{~mol}{ }^{-1}$
B. $-777.7 \mathrm{kjmol}^{-1}$
C. $777.7 \mathrm{kjmol}^{-1}$
D. $-666.6 \mathrm{~kJ} \mathrm{~mol}{ }^{-1}$

## Answer:

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54. The equilibrium constant for the reaction is 10 .

Calculate the value of $\Delta G^{o}$, Given $\mathrm{R}=8 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
, $\mathrm{T}=300 \mathrm{~K}$.

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55. Calculate the entropy change in surrounding when 1.0 mol of $\mathrm{H}_{2} \mathrm{O}(l)$ is formed under standard conditions. Given $\Delta_{f} H^{o}=-286 \mathrm{kJmol}^{-1}$.

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56. Comment on the thermodynamic stability of
$\mathrm{NO}(\mathrm{g})$ and $\mathrm{NO}_{2}(g)$ given :

$$
\begin{aligned}
& \frac{1}{2} N_{2}(g)+\frac{1}{2} O_{2}(g) \rightarrow N O(g), \Delta_{f} H^{o}=90 \mathrm{kJmol}^{-1} \\
& N O(g)+\frac{1}{2} O_{2}(g) \rightarrow N O_{2}(g), \Delta_{f} H^{o}=-74 \mathrm{kJmol}^{-1}
\end{aligned}
$$

57. a) State Hess's Law of constant heat summation.
b) The equilibrium constant for a reaction is 5 . What will be tha value of $\Delta G^{0}$.

Given that $\mathrm{R}=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}, \mathrm{~T}=300 \mathrm{~K}$.
$\mathrm{R}=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$
$T=300 K$

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58. A system in thermodynamics refers to that part of the universe in which observation are made.
a) What do you mean by an isolated system? Given an example.
b) Distinguish between intensive and extensive properties. Give two examples for each.

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59. Lattice enthalpy of an ionic salt is a factor that determine its stability.
a) Define the lattice enthalpy.
b) Draw the Born-Haber cycle for the calculation of lattice enthalpy of the ionic crystal NaCl .
60. The spontaneity of a process is expressed in terms
of a change in Gibbs energy.
a) What is meant by a change in Gibbs energy of a system?
b) How is it related to the enthalpy and entropy of a system?
c) How is it useful in predicting the feasibility of a process?

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61. A spontaneous process is an irreversible process
and may only by reserved by some external agency.
a) Decrese in enthalpy is the only criterion for spontaneity. Do you agree? Why?
b) Calculate the work done for the reversible isothermal expansion of 1 mole of an ideal gas at $27^{\circ} \mathrm{C}$, from a volume of 10 dm to a volume of 20 $d m^{3}$.

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62. Thermodynamics deals with energy changes of macroscopic system.
a) Consider a chemical reaction taking place in a closed insulated vessel. To which type of thermodynamic system does it belong?
b) State the first law of thermodynamics.
c) 3 mol of an ideal gas at 1.5 atm and $25^{\circ} \mathrm{C}$ expands isothermally in a reversible manner to twice its original volume against an external pressure of 1 atm.

Calculate the work done.
$\left[R=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}\right]$

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63. Enthalpy and entropy changes of a reaction are $40.63 \mathrm{~kJ} / \mathrm{mol}$ and $108.8 \mathrm{Jk}^{-1} \mathrm{~mol}^{-1}$. Predict the feasibility of the reaction $\operatorname{atr} 27^{\circ} C$.
64. Most of the naturally occurring processes are spontaneous.
a) Give the criteria for spontaneity of a process in terms of free energy change ( $\Delta G$ )
b) Exothermic reactions associated with a decrease in entropy are sponaneous at lower temperatures.

Justify on the basis of Gibbs equation.
c) Find the temperature above which the reactin
$M g O_{(s)}+C_{(s)} \rightarrow$
$M g_{(s)}+C O_{(g)}$ becomes spontaneous.
(Given
$\left.\Delta_{r} H^{\theta}=490 \mathrm{kJmol}^{-1} \& \Delta_{r} S^{\theta}=198 \mathrm{JKmol}^{-1}\right)$
65. a) The enthalpy of combustion of
$C H_{4(g)}, C_{\text {gradte }}$ and $H_{2(g)}$ at 298 K are -890.3 kJ $\mathrm{mol}^{-1}$, $-393.5 \mathrm{~kJ} \mathrm{~mol}{ }^{-1}$ and $-285.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$ respectively. Calculate the enthalpy of formation of $\mathrm{CH}_{4(\mathrm{~g})}$.
b) Match the following:

$$
\begin{array}{ll}
W=-\Delta u & - \text { Enthaly change } \\
\Delta u=0 & - \text { Universal gas constant } \\
C_{p}-C_{v} & - \text { Adiabatic process } \\
q_{p} & - \text { Isothermal process } \\
& - \text { Cyclic process }
\end{array}
$$

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66. a) For the oxidation of iron 4
$F e_{(s)}+3 O_{2(g)} \rightarrow 2 \mathrm{Fe}_{2} \mathrm{O}_{3(\mathrm{~s})}$, entropy change is
$-549.4 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ at 298 K . Inspite of the negative
entropy change of this reaction, why is the reaction
spontaneous?
( $\Delta H_{r}^{0}$ for the reaction is $-1648 \times 10^{3} \mathrm{Jmol}^{-1}$ ).
b) Write the difference between extensive and intensive properties. Give one example of each.

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67. a) $\Delta G$ gives a criteria for spontaneity of reactions
at a constant pressure and temperature. How is $\Delta G$
helpful in precting the spontaneity of the reaction?
b) State and explain Hess's law of constant heat summation.

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68. a) Classify the following into intensive and extensive properties.
i) Inernal energy ii) Density
iii) Heat Capacity iv) Temperature
b) Calculate the standard free energy change $\left(\Delta G^{\theta}\right)$
for the conversion of oxygen to ozone $\frac{3}{2} O_{3(g)} \rightarrow O_{3(g)}$ at 298 K if the equilibrium
constant for the conversion is $2.47 \times 10^{-29}$.
(Given $\mathrm{R}=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ )

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69. The enthalpy change for the reaction.
$\mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{NH}_{3(\mathrm{~g})}$ is -91.8 kJ at 298
K.what is $\Delta U$ at 298 K ?

$$
\left(R=8.314 J K^{-1} \mathrm{~mol}^{-1}\right)
$$

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70. The enthalpy change in a process is the same, whether the process is carried out in a single step or
inseveral steps.
a) Identify tha law stated here.
b) Calculate the enthalpy of formation of $\mathrm{CH}_{4}$ from the following data :
i) $C_{(s)}+O_{2(g)} \rightarrow \mathrm{CO}_{2(g)}$
$\Delta H=-393.7 \mathrm{~kJ} / \mathrm{mol}$
ii) $\mathrm{H}_{2(g)}+\frac{1}{2} \mathrm{O}_{2(g)} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(l)}$
$\Delta H=-285.8 \mathrm{~kJ} / \mathrm{mol}$
iii) $\mathrm{CH}_{4(g)}+2 \mathrm{O}_{2(g)} \rightarrow \mathrm{CO}_{2(g)}$
$\Delta H=-890.4 \mathrm{~kJ} / \mathrm{mol}$
