Q-1: Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine heat changes
(ii) whose value is independent of the path
(iii) used to determine pressure-volume work
(iv) whose value depends on temperature only

Ans:

(ii) whose value is independent of the path.

Reason:

Functions like pressure, volume and temperature depend on the state of the system only and not on the path.

Q-2: For the process to occur under adiabatic conditions, the correct condition is:
(i) $\Delta T = 0$ (ii) $\Delta p = 0$
(iii) q = 0   (iv) w = 0

Ans:

(iii) q = 0

Reason:

For an adiabatic process, heat transfer is zero, i.e., q = 0.

Q-3: The enthalpies of all elements in their standard states are:

(i) Unity   (ii) Zero

(iii) < 0   (iv) Different for every element

Ans:

(ii) Zero

Q-4: ΔU^0 of combustion of methane is – X kJ mol^{-1}. The value of ΔH^0 is

(i) =

$$\Delta U^{\ominus}$$
(ii) >

$\Delta U^{\ominus}$

(iii) <

$\Delta U^{\ominus}$

(iv) 0

Ans:

(iii) <

$\Delta U^{\ominus}$

Reason:

$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta n_g RT$$

;

$\Delta U^{\ominus}$

= − Y

$kJmol^{-1}$

$$\Delta H^{\ominus} = (-Y) + \Delta n_g RT \Rightarrow \Delta H^{\ominus} < \Delta U^{\ominus}$$

,

Q-5: The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are −890.3 kJ mol⁻¹ − 393.5 kJ mol⁻¹, and −285.8 kJ mol⁻¹, respectively. Enthalpy of the formation of CH$_{4(g)}$ will be

(i) -74.8 kJ

mol^{-1}

(ii) -52.27 kJ

mol^{-1}

(iii) +74.8 kJ

mol^{-1}

(iv) +52 kJ

mol^{-1}

Ans:

(i) -74.8 kJ

mol^{-1}

1. $CH_{4(g)} + 2O_{2(g)}$

$\rightarrow$

$CO_{2(g)} + 2H_2O_{(g)}$

$\Delta H = -890.3 kJ mol^{-1}$

2. $C_{(s)} + O_{2(g)}$

$\rightarrow$

$CO_{2(g)}$

$\Delta H = -393.5 kJ mol^{-1}$

3. $2H_{2(g)} + O_{2(g)}$

$\rightarrow$

$2H_2O_{(g)}$

$\Delta H = -285.8 kJ mol^{-1}$

$C_{(s)} + 2H_{2(g)}$

$\rightarrow$

$CH_{4(g)}$
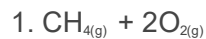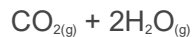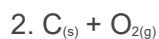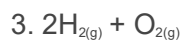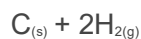
$\Delta_f H_{CH_4}$
=
$\Delta_c H_c$
+
$2\Delta_f H_{H_2}$
–
$\Delta_f H_{CO_2}$

= [-393.5 +2(-285.8) – (-890.3)] kJ

mol^{-1}

= -74.8 kJ

mol^{-1}

Q-6: A reaction, A + B → C + D + q, is found to have a positive entropy change. The reaction will be

(i) possible at high temperature

(ii) possible only at low temperature

(iii) not possible at any temperature

(iv) possible at any temperature

Ans:

(iv) possible at any temperature

ΔG

should be –ve for spontaneous reaction to occur

ΔG
=
ΔH
– T
ΔS

As per the given question,

ΔH

is –ve (as heat is evolved)

ΔS

is +ve
Therefore,

ΔG

is negative
So, the reaction will be possible at any temperature.

Q-7: 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?

Ans:

As per Thermodynamics 1ˢᵗ law,

$$\Delta U$$

= q + W(i);

$$\Delta U$$

internal energy = heat
W = work done

W = -594 J (work done by the system)

q = +701 J (+ve as heat is absorbed)

Now,

$$\Delta U$$
= 701 + (-594)
$$\Delta U$$
= 307 J

Q-8: The reaction of cyanamide, $NH_2CN_{(s)}$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol⁻¹ at 298 K. Calculate the enthalpy change for the reaction at 298 K.

$NH_2CN_{(g)}$ + 3/2 $O_{2(g)}$ → $N_{2(g)}$ + $CO_{2(g)}$ + $H_2O_{(l)}$

Ans:

$$\Delta H$$

is given by,

$$\Delta H = \Delta U + \Delta n_g RT$$
....................(1)
$$\Delta n_g$$

= change in number of moles
$$\Delta n_g$$

= change in number of moles

$$\Delta U$$

= change in internal energy

Here,

$$\Delta n_g = \sum n_g(product) - \sum n_g(reactant)$$
= (2 − 1.5) moles

Δn_g

= 0.5 moles
Here,

T =298 K

ΔU

= -742.7

$kJmol^{-1}$

R =

$8.314 \times 10^{-3} kJmol^{-1}K^{-1}$

Now, from (1)

$$\Delta H = (-742.7 kJmol^{-1}) + (0.5mol)(298K)(8.314 \times 10^{-3} kJmol^{-1}K^{-1})$$

= -742.7 + 1.2

ΔH
= -741.5
$kJmol^{-1}$

Q-9: Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. The molar heat capacity of Al is 24 J mol⁻¹ K⁻¹.

Ans:

Expression of heat(q),

$q = mCP\Delta T$
;......................(a)
ΔT

= Change in temperature
c = molar heat capacity

m = mass of substance

From (a)

$$q = (\tfrac{60}{27} mol)(24 mol^{-1}K^{-1})(20K)$$

q = 1066.67 J = 1.067 KJ

Q-10: Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to the ice at –10.0°C. $\Delta_{fus}H = 6.03$ kJ mol⁻¹ at 0°C.

$$C_p[H_2O_{(l)}] = 75.3J\ mol^{-1}K^{-1}$$

$$C_p[H_2O_{(s)}] = 36.8J\ mol^{-1}K^{-1}$$

Ans:

$$\Delta H_{total}$$

= sum of the changes given below:
(a) Energy change that occurs during the transformation of 1 mole of water from

$$10°C\ to\ 0°C$$

(b) Energy change that occurs during the transformation of 1 mole of water at

$$0°C$$
  to 1 mole of ice at
$$0°C$$

(c) Energy change that occurs during the transformation of 1 mole of ice from

$$0°C\ to\ (-10)°C$$

$$\Delta H_{total} = C_p[H_2OCl]\Delta T + \Delta H_{freezing}C_p[H_2Ol]\Delta T$$
= (75.3

$$Jmol^{-1}K^{-1}$$
)(0 − 10)K + (-6.03*1000
$$Jmol^{-1}$$
(-10-0)K

= -753

$Jmol^{-1}$
− 6030
$Jmol^{-1}$
− 368
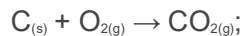$Jmol^{-1}$

= -7151

$Jmol^{-1}$

= -7.151

$kJmol^{-1}$

Thus, the required change in enthalpy for the given transformation is -7.151

$kJmol^{-1}$

Q-11 Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol⁻¹. Calculate the heat released upon the formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Ans:

Formation of carbon dioxide from di-oxygen and carbon gas is given as:

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$;

$\Delta_f H$
= -393.5
$kJmol^{-1}$

1 mole CO_2 = 44g

Heat released during formation of 44g CO_2 = -393.5

$kJmol^{-1}$

Therefore, the heat released during the formation of 35.2g of CO_2 can be calculated as

=

$$\frac{-393.5 kJmol^{-1}}{44g} \times 35.2g$$

= -314.8

$kJmol^{-1}$

Q-12: Enthalpies of formation of CO (g), CO₂ (g), N₂O (g) and N₂O₄(g) are –110, – 393, 81 and 9.7 kJ mol⁻¹, respectively. Find the value of △ᵣH for the reaction:

N₂O₄(g) + 3CO(g)→ N₂O(g) + 3 CO₂(g)

Ans:

"

$\Delta_r H$

for any reaction is defined as the difference between

$\Delta_f H$
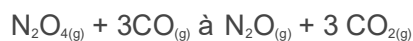
value of products and
$\Delta_f H$

value of reactants."

$$\Delta_r H = \sum \Delta_f H(products) - \sum \Delta_f H(reactants)$$

Now, for

N₂O₄(g) + 3CO(g) à N₂O(g) + 3 CO₂(g)

$$\Delta_r H = [(\Delta_f H(N_2 O) + (3\Delta_f H(CO_2)) - (\Delta_f H(N_2 O_4) + 3\Delta_f H(CO))]$$

Now, substituting the given values in the above equation, we get:

$\Delta_r H$
= [{81
$kJmol^{-1}$
+ 3(-393)
$kJmol^{-1}$
} – {9.7
$kJmol^{-1}$
+ 3(-110)

$kJmol^{-1}$
}]
$\Delta_r H$
= -777.7
$kJmol^{-1}$

Q-13: Given N₂ (g) + 3H₂ (g) → 2NH₃ (g) ; ∆ᵣH°= –92.4 kJ mol⁻¹
What is the standard enthalpy of the formation of NH₃ gas?

Ans:

"Standard enthalpy of formation of a <u>compound</u> is the enthalpy that takes place during the formation of 1 mole of a substance in its standard form, from its constituent elements in their standard state."

Dividing the chemical equation given in the question by 2, we get

$(0.5)N_{2(g)} + (1.5)H_{2(g)} \rightarrow 2NH_{3(g)}$

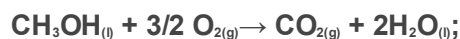Therefore, standard enthalpy for formation of ammonia gas

= (0.5)

$\Delta_r H^{\ominus}$

= (0.5)(-92.4

$kJmol^{-1}$
)

= -46.2

$kJmol^{-1}$

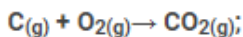**Q-14: Calculate the standard enthalpy of formation of CH₃OH₍ₗ₎ from the following data:**

CH₃OH₍ₗ₎ + 3/2 O₂₍g₎→ CO₂₍g₎ + 2H₂O₍ₗ₎;

$\Delta_r H^{\ominus}$
= -726
$kJmol^{-1}$

$C_{(g)} + O_{2(g)} \rightarrow CO_{2(g)};$

$\Delta_c H_{\ominus}$
= -393
$kJmol^{-1}$

$H_{2(g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(l)};$

$\Delta_f H^{\ominus}$
$= -286$
$kJ mol^{-1}$

Ans:

$C_{(s)} + 2H_2O_{(g)} + (1/2)O_{2(g)} \rightarrow CH_3OH_{(l)}$ …………………………(i)
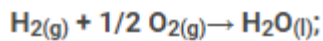
$CH_3OH_{(l)}$ can be obtained as follows,

$\Delta_f H_{\ominus}$
$[CH_3OH_{(l)}] =$
$\Delta_c H_{\ominus}$
2

$\Delta_f H_{\ominus}$
$-$
$\Delta_r H_{\ominus}$

$= (-393$

$kJ mol^{-1}$
$) +2(-286$
$kJ mol^{-1}$
$) - (-726$
$kJ mol^{-1}$
$)$

$= (-393 - 572 + 726)$

$kJ mol^{-1}$

$= -239$

$kJ mol^{-1}$

Thus,

$\Delta_f H_{\ominus}$
$[CH_3OH_{(l)}] = -239$
$kJ mol^{-1}$

Q-15: Calculate the enthalpy change for the process

$CCl_{4(g)} \rightarrow C_{(g)} + 4Cl_{(g)}$ and determine the value of bond enthalpy for C-Cl in $CCl_{4(g)}$.

$\Delta_{vap}H^{\ominus}$
$(CCl_4) = 30.5$
$kJmol^{-1}$
.

$\Delta_f H^{\ominus}$
$(CCl_4) = -135.5$
$kJmol^{-1}$
.

$\Delta_a H^{\ominus}$
$(C) = 715$
$kJmol^{-1}$
,

$\Delta_a H^{\ominus}$
 is a enthalpy of atomisation

$\Delta_a H^{\ominus}$
$(Cl_2) = 242$
$kJmol^{-1}$
.

Ans:

" The chemical equations implying the given values of enthalpies" are:

(1) $CCl_{4(l)}$ à $CCl_{4(g)}$;

$\Delta_{vap}H^{\ominus}$
$= 30.5$
$kJmol^{-1}$

(2) $C_{(s)}$ à $C_{(g)}$

$\Delta_a H^{\ominus}$
$= 715$
$kJmol^{-1}$

(3) $Cl_{2(g)}$ à $2Cl_{(g)}$;

$\Delta_a H^\ominus$
= 242
$kJmol^{-1}$

(4) $C_{(g)}$ + 4$Cl_{(g)}$ à CCl4(g);
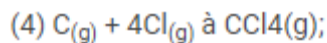
$\Delta_f H^\ominus$
= -135.5
$kJmol^{-1}$
ΔH

for the process $CCl_{4(g)}$ à $C_{(g)}$ + 4$Cl_{(g)}$ can be measured as:

$$\Delta H = \Delta_a H^\ominus(C) + 2\Delta_a H^\ominus(Cl_2) - \Delta_{vap}H^\ominus - \Delta_f H$$

= (715

$kJmol^{-1}$
) + 2(
$kJmol^{-1}$
) − (30.5
$kJmol^{-1}$
) − (-135.5
$kJmol^{-1}$
)

Therefore,

$$H = 1304 kJmol^{-1}$$

The value of bond enthalpy for C-Cl in $CCl_{4(g)}$

=

$\frac{1304}{4} kJmol^{-1}$

= 326

$kJmol^{-1}$

Q-16: For an isolated system, ΔU = 0, what will be ΔS?

Ans:

ΔU
is positive ;
ΔU
> 0.
As

ΔU
$= 0$, then
ΔS

will be +ve, and as a result, the reaction will be spontaneous.

Q-17: For the reaction at 298K,

2A + B → C

ΔH
= 400
$kJmol^{-1}$

ΔH
= 0.2
$kJmol^{-1}K^{-1}$

At what temperature will the reaction become spontaneous considering

ΔS
and
ΔH

to be constant over the temperature range?

Ans:

Now,

$$\Delta G = \Delta H - T\Delta S$$

Let the given reaction is at equilibrium, then

ΔT

will be:
T =

$(\Delta H - \Delta G)\frac{1}{\Delta S}$
$\frac{\Delta H}{\Delta S}$
; (
ΔG

= 0 at equilibrium)
= 400

$kJmol^{-1}$
/0.2
$kJmol^{-1}K^{-1}$

Therefore, T = 2000K
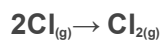
Thus, for the spontaneous,

ΔG

must be –ve and T > 2000K.

Q-18: For the reaction

$2Cl_{(g)} \rightarrow Cl_{2(g)}$

What are the signs of

ΔS
and
ΔH

?
Ans:

ΔS
and
ΔH

are having negative sign.
The reaction given in the question represents the formation of Cl molecules from Cl atoms. As the formation of a bond takes place in the given reaction, energy is released. So,

ΔH

is negative.
Also, 2 moles of Chlorine atoms have more randomness than 1 mole of chlorine molecule. So, the spontaneity is decreased. Thus,

ΔS

is negative.

Q-19: For the reaction
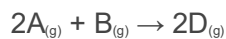
2A$_{(g)}$ + B$_{(g)}$→ 2D$_{(g)}$

$\Delta U^{\ominus}$
= -10.5 kJ and
$\Delta S^{\ominus}$
= -44.1
JK^{-1}

Calculate

$\Delta G^{\ominus}$

for the reaction, and predict whether the reaction may occur spontaneously.

Ans:

2A$_{(g)}$ + B$_{(g)}$ → 2D$_{(g)}$

Δn_g

= 2 – 3
= -1 mole

Putting value of

$\Delta U^{\ominus}$
in expression of
ΔH

:

$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta n_g RT$$
= (-10.5KJ) – (-1)(

$8.314 \times 10^{-3} kJK^{-1}mol^{-1}$
)(298K)

= -10.5kJ -2.48kJ

$\Delta H^{\ominus}$

= -12.98kJ

Putting value of

$\Delta S^{\ominus}$

and

$\Delta H^{\ominus}$

in expression of

$\Delta G^{\ominus}$

:

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

= -12.98kJ −(298K)(-44.1

JK^{-1}

)

= -12.98kJ +13.14kJ

$\Delta G^{\ominus}$

= 0.16kJ

As

$\Delta G^{\ominus}$

is positive, the reaction won't occur spontaneously.

**Q-20: The equilibrium constant for a reaction is 10. What will be the value of ΔG_0? R = 8.314 JK⁻¹ mol⁻
¹, T = 300 K.**

Ans:

Now,

$\Delta G^{\ominus}$

=

$-2.303 RT \ln k$

= (2.303)(

$8.314 \times kJK^{-1} mol^{-1}$

)(300K)

$\log 10$

= -5527

$Jmol^{-1}$

= -5.527

$kJmol^{-1}$

Q-21: Comment on the thermodynamic stability of NO(g), given,

$(1/2)N_{2(g)} + (1/2)O_{2(g)} \rightarrow NO_{(g)}$;

$\Delta_r H^\Theta = 90 kJmol^{-1}$

$NO_{(g)} + (1/2)O_{2(g)} \rightarrow NO_{2(g)}$;

$\Delta_r H^\Theta = -74 kJmol^{-1}$

Ans:

The +ve value of

$\Delta_r H$

represents that during $NO_{(a)}$ formation from O_2 and N_2, heat is absorbed. The obtained product, $NO_{(g),}$ will have more energy than reactants. Thus, $NO_{(g)}$ is unstable.

The -ve value of

$\Delta_r H$

represents that during $NO_{2(a)}$ formation from $O_{2(g)}$ and $NO_{(g)}$, heat is evolved. The obtained product, $NO_{2(g),}$ gets stabilised with minimum energy.
Thus, unstable $NO_{(g)}$ converts into stable $NO_{2(g).}$

-22: Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta_f H^o = -286$ kJ mol^{-1}.

Ans:

$\Delta_r H^\Theta = -286 kJmol^{-1}$

is given, so that amount of heat is evolved during the formation of 1 mole of $H_2O_{(l)}$.
Thus, the same heat will be absorbed by surrounding Q_{surr} = +286

$kJmol^{-1}$

.

Now,

ΔS_{surr}

$= Q_{surr}/7$

$=$

$\dfrac{286kJmol^{-1}}{298K}$

Therefore,

$\Delta S_{surr} = 959.73Jmol^{-1}K^{-1}$