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° of combustion of methane is – X kJ mol^{-1}. The value of ΔH° is

(i) =

ΔU^{Θ}

(ii) >

ΔU^{Θ}

(iii) <

ΔU^{Θ}

(iv) 0

Ans:

(iii) **<**

ΔU^{Θ}

Reason:

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

;

ΔU^{Θ}

= – Y

$kJmol^{-1}$

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

,

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,

ΔU

= q + W(i);

ΔU

internal energy = heat
W = work done

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

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

Now,

ΔU
= 701 + (-594)
ΔU
= 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.

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

Ans:

ΔH

is given by,

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

= change in number of moles
Δn_g

= change in number of moles

ΔU

= 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)

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

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

$$10^oC\ to\ 0^oC$$

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

$$0^oC$$

to 1 mole of ice at

$$0^oC$$

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

$$0^oC\ to\ (-10)^oC$$

$$\Delta H_{total} = C_p[H_2OCl]\Delta T + \Delta H_{freezing} C_p[H_2O_l]\Delta T$$

= (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

=

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

= -314.8

$kJmol^{-1}$

Q-12: Enthalpies of formation of CO $_{(g)}$, $CO_{2\,(g)}$, $N_2O_{(g)}$ and $N_2O_{4(g)}$ are –110, – 393, 81 and 9.7 kJ mol^{-1}, respectively. Find the value of $\triangle_r H$ for the reaction:

$N_2O_{4(g)}$ + 3$CO_{(g)}$⟶ $N_2O_{(g)}$ + 3 $CO_{2(g)}$

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

$N_2O_{4(g)}$ + 3$CO_{(g)}$ à $N_2O_{(g)}$ + 3 $CO_{2(g)}$

$$\Delta_r H = [(\Delta_f H(N_2O) + (3\Delta_f H(CO_2)) - (\Delta_f H(N_2O_4) + 3\Delta_f H(CO))]$$

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 N_2 (g) + $3H_2$ (g) → $2NH_3$ (g) ; $\Delta_r H^0$= –92.4 kJ mol^{-1}
What is the standard enthalpy of the formation of NH_3 gas?

Ans:

"Standard enthalpy of formation of a compound 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)

$\Delta_r H^{\Theta}$

= (0.5)(-92.4

$kJmol^{-1}$
)

= -46.2

$kJmol^{-1}$

Q-14: Calculate the standard enthalpy of formation of $CH_3OH_{(l)}$ from the following data:

$CH_3OH_{(l)}$ + 3/2 $O_{2(g)}$→ $CO_{2(g)}$ + $2H_2O_{(l)}$;

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

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

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

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

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

Ans:

$C_{(s)} + 2H_2O_{(g)} + (1/2)O_{2(g)} \rightarrow CH_3OH_{(l)}$ .....(i)

$CH_3OH_{(l)}$ can be obtained as follows,

$\Delta_f H_{\Theta}[CH_3OH_{(l)}] = \Delta_c H_{\Theta}$ 2 $\Delta_f H_{\Theta}$ – $\Delta_r H_{\Theta}$

= (-393 $kJmol^{-1}$) +2(-286 $kJmol^{-1}$) – (-726 $kJmol^{-1}$)

= (-393 – 572 + 726) $kJmol^{-1}$

= -239 $kJmol^{-1}$

Thus,

$\Delta_f H_{\Theta}[CH_3OH_{(l)}]$ = -239 $kJmol^{-1}$

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 $CCl_{4(g)}$.

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

$\Delta_{f}H^{\Theta}$
(CCl_4) = -135.5
$kJmol^{-1}$
.

$\Delta_{a}H^{\Theta}$
(C) = 715
$kJmol^{-1}$
,

$\Delta_{a}H^{\Theta}$
is a enthalpy of atomisation

$\Delta_{a}H^{\Theta}$
(Cl_2) = 242
$kJmol^{-1}$
.

Ans:

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

(1) $CCl_{4(l)}$ à $CCl_{4(g)}$;

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

(2) $C_{(s)}$ à $C_{(g)}$

$\Delta_{a}H^{\Theta}$
= 715
$kJmol^{-1}$

(3) $Cl_{2(g)}$ à $2Cl_{(g)}$;

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

(4) $C_{(g)} + 4Cl_{(g)}$ à CCl4(g);

$\Delta_f H^\Theta$
= -135.5
$kJmol^{-1}$
ΔH

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

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

= (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, ∆U = 0, what will be ∆S?

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

$2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$

ΔU^{Θ}
= -10.5 kJ and
ΔS^{Θ}
= -44.1
JK^{-1}

Calculate

ΔG^{Θ}

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

Ans:

$2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$

Δn_g

= 2 – 3
= -1 mole

Putting value of

ΔU^{Θ}
in expression of
ΔH

:

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

= (-10.5KJ) – (-1)(

$8.314 \times 10^{-3} kJK^{-1}mol^{-1}$

)(298K)

= -10.5kJ -2.48kJ

ΔH^{Θ}
= -12.98kJ
Putting value of

ΔS^{Θ}
and
ΔH^{Θ}
in expression of
ΔG^{Θ}
:

$\Delta G^{\Theta} = \Delta H^{\Theta} - T\Delta S^{\Theta}$
= -12.98kJ −(298K)(-44.1

JK^{-1}
)

= -12.98kJ +13.14kJ

ΔG^{Θ}
= 0.16kJ
As

ΔG^{Θ}
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,

ΔG^{Θ}
=
$-2.303RT \ln k$
= (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,

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

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

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

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

Ans:

The +ve value of

$\Delta_r H$

represents that during $NO_{(g)}$ 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 $NO_{2(g)}$ 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. $\Delta_f H^0 = -286$ kJ mol^{-1}.

Ans:

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

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}

= $Q_{surr}/7$

=

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

Therefore,

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