

Q-1: Choose the correct answer	A thermodynamic state	function is a quantity
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- (i) used to determine heat changes
- (ii) whose value is independent of path
- (iii) used to determine pressure volume work
- (iv) whose value depends on temperature only

Ans:

(2) A quantity which is independent of path.

Reason:

Functions like pressure, volume and temperature depends 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:

3: 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:

- (1) Zero
- (2) < 0
- (3) Different for every element
- (4) Unity

Ans:

(1) Zero

Q-4: AU

0

of combustion of methane is - X kJ mol-1. The value of AH0 is

(a) >
$$\Delta U^{\Theta}$$

(b) =
$$\Delta U^{\Theta}$$

- (c) = 0
- (d) < ΔU^{Θ}

Ans:

(d) < ΔU^{Θ}



Reason:

$$\Delta H^{\Theta} = \, \Delta U^{\Theta} + \, \Delta n_q RT$$
 ; 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 formation of CH4 (g) will be

- (a) -52.27kJ mol^{-1}
- (b) $52kJ mol^{-1}$
- (c) +74.8kJ mol^{-1}
- (d) -74.8kJ mol^{-1}

Ans:

(d) -74.8
$$\mathrm{kJ} mol^{-1}$$

à
$$CH_{4(q)} + 2O_{2(q)} \rightarrow CO_{2(q)} + 2H_2O_{(q)}$$

$$\Delta H = -890.3kJmol^{-1}$$

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

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

à
$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$$

$$\Delta H = -285.8k.Imol^{-1}$$

à
$$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$$

$$\Delta_f H_{CH_4} = \Delta_c H_c + 2\Delta_f H_{H_2} - \Delta_f H_{CO_2}$$

= [-393.5 +2(-285.8) - (-890.3)]
$${\rm kJ} mol^{-1}$$



= -74.8kJ
$$mol^{-1}$$

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

- (a) will be possible at low temperature only
- (b) will be possible at high temperature only
- (c) will be possible at any temperature
- (d) won't be possible at any temperature

Ans:

(c) will be possible at any temperature

 ΔG should be -ve, for spontaneous reaction to occur

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

As per given in question,

 ΔH is -ve (as heat is evolved)

$$\Delta S$$
 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,

$$\Delta U = q + W(i);$$

 ΔU internal energy = heat

W = work done

W = -594 J (work done by system)

q = +801 J (+ve as heat is absorbed)

Now,

$$\Delta U = 801 + (-594)$$

$$\Delta U = 207 \text{ J}$$



Q-8: The reaction of cyanamide, NH2CN (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 enthalpy change for the reaction at 298 K.

$$NH_2CN_{(g)} + 3/2O_{2(g)} a N_{2(g)} + CO_{2(g)} + H_2O_{(1)}$$

Ans:

 ΔH is given by,

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

 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 - 2.5) moles

$$\Delta n_g$$
 = -0.5 moles

Here.

T = 298K

$$\Delta U = -753.7 \ kJmol^{-1}$$

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

Now, from (1)

$$\Delta H = (-753.7kJmol^{-1}) + (-0.5mol)(298K)(8.314 \times 10^{-3}kJmol^{-1}K^{-1})$$
= -753.7 - 1.2

$$\Delta H$$
 = -754.9 $kJmol^{-1}$

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. 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)

$$q=(rac{50}{27}mol)(24mol^{-1}K^{-1})(20K)$$

q = 888.88 J q

Q-10: Calculate the enthalpy change on freezing of 1.0 mol of water at10.0°C to ice at −10.0°C. ∆fusH = 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:

 ΔH_{total} = sum of the changes given below:

- (a) Energy change that occurs during transformation of 1 mole of water from $10^{\circ}C$ to $0^{\circ}C$.
- (b) Energy change that occurs during transformation of 1 mole of water at $0^{\circ}C$ to 1 mole of ice at

 $0^{\circ}C$.

(c) Energy change that occurs during transformation of 1 mole of ice from $0^{\circ}C$ to $(-10)^{\circ}C$.

$$\Delta H_{total} = C_p[H_2OCl]\Delta T + \Delta H_{freezing}C_p[H_2O_s]\Delta T$$

=
$$(75.3 \ Jmol^{-1}K^{-1})(0-10)K + (-6.03*1000 \ Jmol^{-1}(-10-0)K)$$

$$= -753 \ Jmol^{-1} - 6030 \ Jmol^{-1} - 368 \ Jmol^{-1}$$

= -7151
$$Jmol^{-1}$$

= -7.151
$$kJmol^{-1}$$

Thus, the required change in enthalpy for given transformation is -7.151 $kJmol^{-1}$.



Q-11: 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 $\triangle rH$ for the reaction:

$$N_2O_{4(q)} + 3CO_{(q)} \grave{a} N_2O_{(q)} + 3CO_{2(q)}$$

Ans:

" $\Delta_r H$ for any reaction is defined as the fifference 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

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

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

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

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

$$-777.7 \ kJmol^{-1}$$

Q-12 Enthalpy of combustion of carbon to CO2 is -393.5 kJ mol-1. Calculate the heat released upon formation of 35.2 g of CO2 from carbon and dioxygen gas.

Δns

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

$$C_{(s)} + O_{2(g)}$$
 à $CO_{2(g)}$; $\Delta_f H = -393.5 \ kJmol^{-1}$

1 mole $CO_2 = 44q$

Heat released during formation of 44g CO₂ = -393.5 $kJmol^{-1}$

Therefore, heat released during formation of 37.2g of CO₂ can be calculated as

$$=\frac{-393.5kJmol^{-1}}{44g}\times 37.2g$$

$$= -332.69 \ k.Imol^{-1}$$

Q-13: Given N2 (g) + 3H2 (g) \rightarrow 2NH3 (g) ; $\triangle_r H^0 = -92.4$ kJ mol⁻¹ What is the standard enthalpy of formation of NH3 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)
$$\Delta_r H^{\Theta}$$

$$= (0.5)(-92.4 kJmol^{-1})$$

$$=-46.2kJmol^{-1}$$

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

$${\rm CH_{3}OH_{(I)} + (3/2)O_{2(g)}\grave{a}~CO_{2(g)} + 2H_{2}O_{(I)};~\Delta_{r}H^{\Theta} = \text{-726}~kJmol^{-1}}$$

$$C_{(q)} + O_{2(q)} a CO_{2(q)}$$
; $\Delta_c H_{\Theta} = -393 \ kJmol^{-1}$

$$H_{2(g)} + (1/2)O_{2(g)} \dot{a} H_2O_{(l)}; \Delta_f H^{\Theta} = -286 \ kJmol^{-1}$$

Ans:

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

$$\Delta_f H_\Theta$$
 [CH₃OH_(I)] = $\Delta_c H_\Theta$

$$2\Delta_f H_\Theta$$
 - $\Delta_r H_\Theta$

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

$$= (-393 - 572 + 726) kJmol^{-1}$$

=
$$-239 kJmol^{-1}$$

Thus,
$$\Delta_f H_\Theta$$
 [CH $_3$ OH $_{(|)}$] = -239 $kJmol^{-1}$

Q-15: Calculate the enthalpy change for the process

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

$$\Delta_{vap}H^{\Theta}$$
 (CCI₄) = 30.5 $kJmol^{-1}$.

$$\Delta_f H^\Theta$$
 (CCI₄) = -135.5 $kJmol^{-1}$.



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

 $\Delta_a H^\Theta$ is a enthalpy of atomisation

$$\Delta_a H^{\Theta}$$
 (Cl₂) = 242 $kJmol^{-1}$.

Ans:

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

(1)
$$\mathrm{CCl}_{4(l)}$$
 à $\mathrm{CCl}_{4(g)}$; $\Delta_{vap}H^\Theta$ = 30.5 $kJmol^{-1}$

(2)
$$C_{(s)}$$
 à $C_{(g)}$ $\Delta_a H^\Theta$ = 715 $kJmol^{-1}$

(3)
$$\operatorname{Cl}_{\operatorname{2(g)}}$$
 à $\operatorname{2Cl}_{\operatorname{(g)}}$; $\Delta_a H^\Theta$ = 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:

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

=
$$(715kJmol^{-1}) + 2(kJmol^{-1}) - (30.5kJmol^{-1}) - (-135.5kJmol^{-1})$$

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

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

$$= \frac{1304}{4} k J mol^{-1}$$

$$= 326 \ kJmol^{-1}$$

Q-16: For an isolated system, $\Delta U = 0$, what will be ΔS ?

Ans:

$$\Delta U$$
 is positive; $\Delta U > 0$.

As, ΔU = 0 then ΔS will be +ve, as a result reaction will be spontaneous.



Q-17:

Following reaction takes place at 298K,

2X + Y à Z

$$\Delta H$$
 = 400 $kJmol^{-1}$

$$\Delta H = 0.2 \, k \, Jmol^{-1} \, K^{-1}$$

Find the temperature at which the reaction become spontaneous considering ΔS and ΔH to be constant over the entire 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: 2Cl(g)à Cl2(g)

In above reaction what can be the sign for ΔS and ΔH ?

Ans:

 ΔS and ΔH are having negative sign.

The reaction given in the question represents the formation of CI molecule from CI atoms. As the formation of bond takes place in the given reaction. So, energy is released. So, ΔH is negative.

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

Q-19:
$$2X_{(g)} + Y_{(g)} a 2D_{(g)}$$



$$\Delta U^{\Theta}$$
 = -10.5 kJ and ΔS^{Θ} = -44.1 JK^{-1}

Determine ΔG^{Θ} for the given reaction, and predict that whether given reaction can occur

spontaneously or not.

Ans:

$$2X_{(g)} + Y_{(g)} à 2D_{(g)}$$

$$\Delta n_a$$
 = 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

$$\Delta H^{\Theta}$$
 = -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
$$-(298K)(-44.1JK^{-1})$$

$$\Delta G^{\Theta} = 0.16 \text{kJ}$$

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 \triangle G0? R = 8.314 JK-1 mol-1, T = 300 K.

Ans:

Now,

$$\Delta G^{\Theta} = -2.303 RT \log eq$$
 = (2.303)($8.314 \times 10^{-3} kJK^{-1} mol^{-1}$)(300K) $\log 10$



$$= -5744.14 Jmol^{-1}$$

$$-5.744 \, kJmol^{-1}$$

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

$$(1/2)N_{2(q)} + (1/2)O_{2(q)}; \Delta_r H^{\Theta} = 90kJmol^{-1}$$

NO_(q) + (1/2)O_{2(q)}à NO_{2(q)} ;
$$\Delta_r H^\Theta = -74kJmol^{-1}$$

Ans:

The +ve value of $\Delta_r H$ represents that during NO_(g) formation from O₂ and N₂, heat is absorbed. The obtained product, NO_(q) is having more energy than reactants. Thus, NO_(q) 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 stabilized with minimum energy.

Thus, unstable NO(q) converts into unstable NO2(q).

Q-22: Calculate the entropy change in surroundings when 1.00 mol of H2O(I) is formedunder standard conditions. $\Delta_f H^0 = -286 \text{ kJ mol}^{-1}$.

Ans:

$$\Delta_r H^\Theta = -286 kJmol^{-1}$$
 is given so that amount of heat is evolved during the formation of 1 mole of H2O(I).

Thus, the same heat will be absorbed by surrounding. Q $_{
m surr}$ = +286 $kJmol^{-1}$.

Now,
$$\Delta S_{surr}$$
 = Q_{surr}/7

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