THERMOCHEMISTRY

1. Given :

(i) $C(graphite) + O_2(g) \rightarrow CO_2(g)$;
$\Delta rH^\circ = x\ kJ\ mol^{-1}$

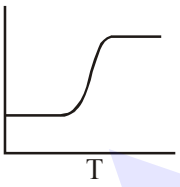
(ii) $C(graphite) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$;
$\Delta rH^\circ = y\ kJ\ mol^{-1}$

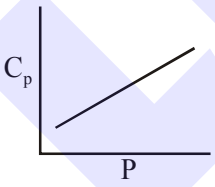
(iii) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$;
$\Delta rH^\circ = z\ kJ\ mol^{-1}$

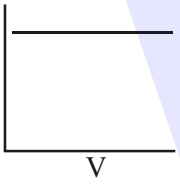
Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct ?

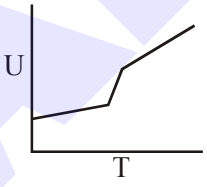
(1) $z = x + y$ (2) $x = y - z$
(3) $x = y + z$ (4) $y = 2z - x$

2. For diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities ?

(1) 

(2) 

(3) 

(4) 

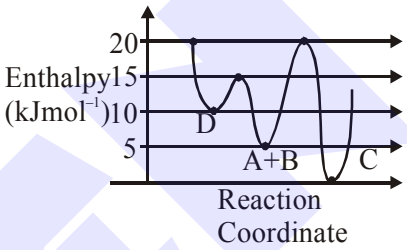
3. The process with negative entropy change is :

(1) Dissolution of iodine in water
(2) Synthesis of ammonia from N_2 and H_2
(3) Dissolution of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$
(4) Subimation of dry ice

4. Consider the given plot of enthalpy of the following reaction between A and B.

$A + B \rightarrow C + D$

Identify the incorrect statement.



(1) C is the thermodynamically stable product.
(2) Formation of A and B from C has highest enthalpy of activation.
(3) D is kinetically stable product.
(4) Activation enthalpy to form C is 5kJ mol^{-1} less than that to form D.

5. Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C. If specific heat of $I_2(s)$ and $I_2(vap)$ are 0.055 and 0.031 cal $g^{-1}K^{-1}$ respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is :

(1) 2.85 (2) 11.4
(3) 5.7 (4) 22.8

6. The difference between ΔH and ΔU ($\Delta H - \Delta U$), when the combustion of one mole of heptane (1) is carried out at a temperature T, is equal to:

(1) 3RT (2) –3RT
(3) –4RT (4) 4RT

SOLUTION

1. Ans. (3)

$$C_{(graphite)} + O_2(g) \rightarrow CO_2(g)\Delta_r H^\circ = xkJ/mol \quad ...(1)$$

$$C_{(graphite)} + \frac{1}{2}O_2(g) \rightarrow CO(g)\Delta_r H^\circ = ykJ/mol \quad ...(2)$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)\Delta_r H^\circ = zkJ/mol \quad ...(3)$$

(1) = (2) + (3)

x = y + z

2. Ans. (2)

At higher temperature, rotational degree of freedom becomes active.

$$C_P = \frac{7}{2}R \quad \text{(Independent of P)}$$

$$C_V = \frac{5}{2}R \quad \text{(Independent of V)}$$

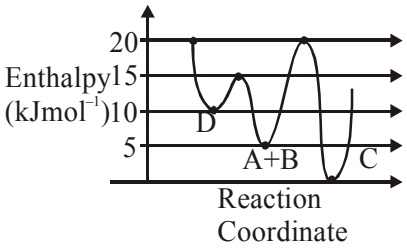
Variation of U vs T is similar as C_V vs T

3. Ans. (2)

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta n_g < 0$

4. Ans. (4)

Sol. $A + B \rightarrow C + D$



Activation enthalpy for C = 20 – 5 = 15kJ/mol

Activation enthalpy for D = 15 – 5 = 10kJ/mol.

5. Ans. (4)

Sol. $I_{2(s)} \rightarrow I_{2(g)}$: ΔH_1 = 24 cal/g at 200°C

$\Delta H_2 = \Delta H_1 + \Delta C_{P_{rxn}} (T_2 - T_1)$

= 24 + (0.031 –0.055) × 50

= 24–1.2

= 22.8 Cal/g

6. Ans. (3)

Sol. $C_7H_{16}(\ell) + 11O_2(g) \longrightarrow 7CO_2(g) + 8H_2O(\ell)$

$\Delta n_g = n_p - n_r = 7 - 11 = -4$

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

$\therefore \Delta H - \Delta U = -4\ RT$