

Thermodynamics



TRY YOURSELF

ANSWERS

1. $\Delta U = q + w$

' q ' and ' w ' are not state functions because they are path dependent.

Since, ΔU does not depend on path and it is equal to $(q + w)$, therefore, $(q + w)$ or ΔU is state function.

2. For isothermal reversible work,

$$w = -2.303 nRT \log \left(\frac{V_2}{V_1} \right)$$

$$= -2.303 \times 0.5 \times 8.314 \times 300 \log \left(\frac{35}{25} \right) = -419.7 \text{ J}$$

(-ve sign represents work done by the gas during expansion)

3. We know, $w = -2.303nRT \log \left(\frac{V_2}{V_1} \right)$

$$-4754 = -2.303 \times n \times 8.314 \times 300 \log \left(\frac{20}{10} \right)$$

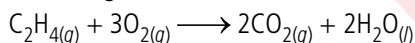
$$n = 2.75 \text{ mol}$$

4. According to first law of thermodynamics, $\Delta U = q + w$

When $\Delta U = 0$, i.e., for isothermal process, $q = -w$

i.e., heat absorbed by the system is equal to work done.

5. The given reaction is



$$\Delta n_g = 2 - 4 = -2$$

$$\text{We know, } \Delta H = \Delta U + \Delta n_g RT$$

$$-1410 \times 10^3 = \Delta U + (-2) \times 8.314 \times 298$$

$$-1410 \times 10^3 = \Delta U - 4955.14$$

$$\Delta U = -1405044.8 \text{ J} = -1405.04 \text{ kJ}$$

6. (i) Heat capacity of the system is defined as the quantity of heat required to raise the temperature of the system by one degree. This is denoted by C_v (at constant volume) and

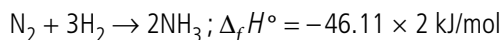
C_p (at constant pressure). So, heat capacity = $\frac{dq}{dT}$

$$(ii) C_p - C_v = nR = 10R = 10 \times 8.314 = 83.14 \text{ J K}^{-1}$$

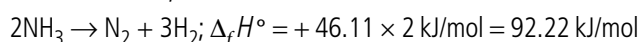
7. Molar heat capacity = Molar mass \times Specific heat
 $= 124 \times 0.757 = 93.868 \text{ J K}^{-1} \text{ mol}^{-1}$.

8. Hess's law is found very useful in calculating the enthalpy change for the reaction for which experimental determination is not possible.

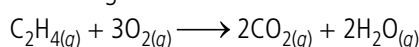
9. $\frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightarrow \text{NH}_3; \Delta_f H^\circ = -46.11 \text{ kJ/mol}$



For the reaction,



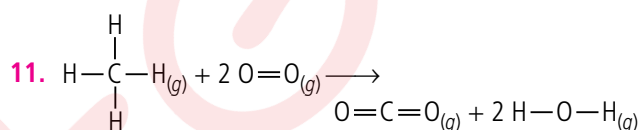
10. The given reaction is :



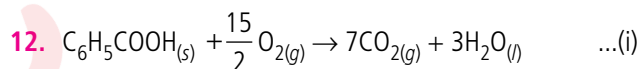
$$\Delta_f H^\circ = [2\Delta_f H^\circ_{\text{CO}_2} + 2\Delta_f H^\circ_{\text{H}_2\text{O}}] - [\Delta_f H^\circ_{\text{C}_2\text{H}_4} + 3\Delta_f H^\circ_{\text{O}_2}]$$

$$\text{or } -1323 = [2 \times (-393.5) + 2(-249)] - [x + 3 \times 0]$$

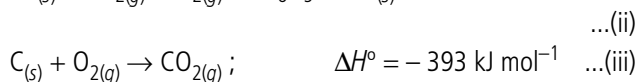
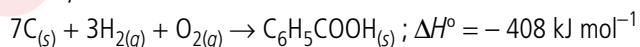
$$\Rightarrow x = 38 \text{ kJ/mol}$$



$$\begin{aligned} \Delta H &= B.E._{(\text{reactants})} - B.E._{(\text{products})} \\ &= 4 B.E._{\text{C-H}} + 2 B.E._{\text{O=O}} - 2 B.E._{\text{C=O}} - 4 B.E._{\text{O-H}} \\ &= 4 \times 414 + 2 \times 498 - 2 \times 741 - 4 \times 464 \\ &= (1656 + 996 - 1482 - 1856) = -686 \text{ kJ mol}^{-1} \end{aligned}$$



Given,



eqn. (i) is obtained as : $7 \times (iii) + 3 \times (iv) - (ii)$

$$\Delta H^\circ = [-393 \times 7 - 286 \times 3 + 408]$$

$$\therefore \Delta H^\circ = -3201 \text{ kJ mol}^{-1}$$

$$\text{Also } \Delta H_p = \Delta H_v + \Delta n_g RT$$

$$\therefore -3201 = \Delta H_v + (-1/2) \times 8.314 \times 10^{-3} \times 300$$

$$(\because \Delta n_g = -1/2 \text{ and } R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})$$

$$\therefore \Delta H_v = -3201 + 1.2471 = -3199.7529 \text{ kJ mol}^{-1}$$

13. 1 mole of CO = 28 g

$$\Delta_{\text{vap}} H \text{ for CO} = 6.04 \text{ kJ mol}^{-1}$$

Enthalpy change for vaporisation of 28 g CO = 6.04 kJ

Enthalpy change for vaporisation of 5.6 g CO

$$= \frac{6.04}{28} \times 5.6 = 1.208 \text{ kJ}$$

14. $\Delta_{\text{fus}} H = 6.025 \times 1000 = 6025 \text{ J mol}^{-1}$

$$= \frac{6025}{18} \text{ J g}^{-1} = 334.72 \text{ J g}^{-1}$$

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T_f} = \frac{334.72}{273} = 1.226 \text{ J K}^{-1} \text{ g}^{-1}$$

15. We know,

$$\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T_b} = \frac{29 \times 1000}{341.7} = 84.87 \text{ J K}^{-1} \text{ mol}^{-1}$$

16. Solid is less random than liquid which in turn is less random than gas. For the same state, at the same pressure, higher the temperature, greater is the randomness. Hence the order is (b) < (d) < (c) < (a).

17. Given: $\Delta S = 3 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$

$$\Delta H = -300 \text{ kJ mol}^{-1} = -300 \times 10^3 \text{ J mol}^{-1}$$

$$\therefore \Delta G = \Delta H - T\Delta S = -300 \times 10^3 - 300 \times 3 = -300900 \text{ J} \\ = -300.9 \text{ kJ mol}^{-1}$$

18. (a) Under ordinary conditions, the average energy of the reactants may be less than the threshold energy. They require some activation energy to initiate the reaction.

$$(b) \Delta G = \Delta H - T\Delta S$$

At lower temperature, if value of ΔH is negative ΔG will be -ve and if ΔH is positive, ΔG will be positive. While at higher temperature $-T\Delta S$ will be high, thus, sign of ΔS will decide whether ΔG will be positive or negative.

19. Here, we are given

$$\Delta_f G^\circ (\text{NH}_3) = -16.8 \text{ kJ mol}^{-1},$$

$$\Delta_f G^\circ (\text{NO}) = +86.7 \text{ kJ mol}^{-1},$$

$$\Delta_f G^\circ (\text{H}_2\text{O}) = -237.2 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \therefore \Delta_r G^\circ &= \sum \Delta_f G^\circ_{(\text{products})} - \sum \Delta_f G^\circ_{(\text{reactants})} \\ &= [4 \times \Delta_f G^\circ (\text{NO}) + 6 \times \Delta_f G^\circ (\text{H}_2\text{O})] \\ &\quad - [4 \times \Delta_f G^\circ (\text{NH}_3) + 5 \Delta_f G^\circ (\text{O}_2)] \\ &= [4 \times (86.7) + 6 \times (-237.2)] - [4 \times (-16.8) + 5 \times 0] \\ &= -1009.2 \text{ kJ} \end{aligned}$$

Since, $\Delta_r G^\circ$ is negative, hence the process is feasible.

$$\begin{aligned} 20. (i) \Delta G &= \Delta G_{\text{product}} - \Delta G_{\text{reactant}} \\ &= 2 \times \Delta G_{\text{HCl}} - 2 \times \Delta G_{\text{HI}} = 2 \times (-95.2) - 2 \times 1.8 \\ &= -194 \text{ kJ/mol} \end{aligned}$$

Reaction will proceed spontaneously because ΔG for the reaction has negative value.

$$\begin{aligned} (ii) \Delta G &= \Delta G_{\text{product}} - \Delta G_{\text{reactant}} \\ &= 2 \times \Delta G_{\text{HI}} - \Delta G_{\text{H}_2} \\ &= (2 \times 1.8) - (-33.8) = 37.4 \text{ kJ/mol} \end{aligned}$$

Reaction will not be spontaneous because ΔG is positive for the reaction. Elevation of temp. will retard reaction (i) (exothermic) while the reaction (ii) (endothermic) will be encouraged.

