SOLUTION

EXERCISE O-I

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1. $C(graphite,s) + \frac{3}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow CH_3Cl(g)$

2. $\Delta rH = -944.7 - 4 \times 92.3 + 763.2 + 2 \times 241.8 = -67.1$ kJ

3. $-890.4 = -393.5 - 2 \times 285.9 - \Delta H_f + CH_4(g)$

$\Delta H_f\, CH_4(g) = -74.9$ kJ

4. $-40 = 2\Delta H_f\, NH_3 - \Delta H_f\, N_2H_4(g)$

$-40 = 2\, \Delta H_f\, NH_3(g) + 120$

$2\Delta H_f\, NH_3(g) = -160 \Rightarrow \Delta H_f\, NH_3(g) = -80$ kJ

5. $-2601 = -4 \times 394 - 2 \times 285.8 - 2\, \Delta H_f\, C_2H_2$

$2\Delta H_f\, C_2H_2 = 453.4$

$\Delta H_f\, C_2H_2 = 226.7$ kJ

6. $\Delta H_f\, HCl(g) = \frac{\Delta H_3}{2}$

$\Delta H_f\, NH_3(g) = \frac{\Delta H_2}{2}$

$-\Delta H_1 = \Delta H_f\, NCl_3(g) + 3\Delta H_f\, HCl(g) - \Delta H_f\, NH_3(g)$

$-\Delta H_1 = \Delta H_f\, NIl_3(g) + \frac{3}{2} \Delta H_3 - \frac{\Delta H_2}{2}$

$\Delta H_f\, NCl_3(g) = \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3 - \Delta H_1$

7. $A \longrightarrow B \quad \Delta H = +100$ Kcal

$\Delta H_f\, B > \Delta H_f\, A$

$B \longrightarrow C \quad \Delta H = -80$ Kcal

$\Delta H_f\, B > \Delta H_f\, C$

$A \longrightarrow C \quad \Delta H = +20$ Kcal

$\Delta H_f\, C > \Delta H_f\, A$

$\Rightarrow \Delta H_f\, B > \Delta H_f\, C > \Delta H_f\, A$

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8. $C_3H_8(g) + SO_2(g) \longrightarrow 3CO_2(g) + 4\,H_2O(l)$

$-2221.6 = -3 \times 394 - 4 \times 285.8 - \Delta H_f\, C_3H_8(g)$

$\Delta H_f\, C_3H_8(g) = 103.6$ kJ

$$\Delta U_f^0\ NO_2(g) = -\frac{0.5\times 2\times 1000}{1000} = +8 \text{ Kcal mol}^{-1}$$

9. $$\Delta H = -\frac{1939.1}{40}\times 12 = -1939.1 \times 0.3 \text{ kJ} = -581.73 \text{ kJ}$$

10. $2H(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(g)$

$H_2(g) + \frac{1}{2}\,O_2(g) \xrightarrow{-242} H_2O(g)$

Resonating R.H. Structure

$6C(g) + 6H(g) \xrightarrow{-5530}$

$= -242$

$\Delta rH_1 = -678$ kJ

$$\frac{\Delta rH_1}{\Delta rH_2} = \frac{678}{242} = 2.8$$

11. from **(d)** $\Delta H_f\, H_2O(\ell) = -285$ kJ

(a) $2NH_3(g) + 3N_2O(g) \longrightarrow 4N_2(g) + 3H_2O(\ell)$ $\Delta rH = -1011$ kJ

$3\Delta H_f\, H_2O(\ell) - 2\Delta H_f\, NH_3(g) - 3\Delta H_f\, N_2O(g) = -1011$

$2\Delta H_f\, NH_3(g) + 3\Delta H_f\, N_2O(g) = -3 \times 285 + 1011 = 156$ (i)

(b) $N_2O(g) + 3H_2(g) \longrightarrow N_2H_4(\ell) + H_2O(\ell)$ $\Delta rH = -317$ kJ

$\Delta H_f\, N_2H_4(\ell) - \Delta H_f\, N_2O(g) + \Delta H_f\, H_2O(\ell) = -317$ kJ

$\Delta H_f\, N_2H_4(\ell) - \Delta H_f\, N_2O(g) = -32$ (ii)

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(c) $4NH_3(g) + O_2(g) \longrightarrow 2N_2H_4(\ell) + 2H_2O(\ell)$ $\Delta rH = -286$ kJ

$2\Delta H_f\, N_2H_4(\ell) + 2\Delta H_f\, H_2O(\ell) - 4\Delta H_f\, NH_3(g) = -286$ kJ

$2\Delta H_f\, N_2H_4(\ell) - 4\Delta H_f\, NH_3(g) = 284$ (iii)

from (i), (iii) and (iii)

$\Delta H_f\, N_2H_4(\ell) = 50.5$ kJ/mol

$\Delta H_f\, N_2O(g) = 82.5$ kJ/mol

$\Delta H_f\, NH_3(g) = -45.75$ kJ/mol

$\Delta rH = 3\Delta H_f\, H_2O(\ell) - \Delta H_f\ N_2H_4(\ell)$

$= -3 \times 285 - 50.5$

$= -620.5$ kJ/mol

12. (i) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

$\Delta rH_{300K} = -184.5$

(ii) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

$\Delta rH_{300K} = -483$ kJ/mol

(iii) $4HCl(g) + O_2(g) \longrightarrow 2Cl_2(g) + 2H_2O(g)$

(iii) = (ii) − 2 × (i)

$\Delta rH_3 = \Delta rH_2 - 2 \times \Delta rH_1 = -483 + 2 \times 184.5 = -114$ kJ/mol

$\Delta H = \Delta U + \Delta ng\, RT$

$$-114 = \Delta U + \frac{-1 \times 8.3 \times 300}{1000}$$

$\Delta U = -111.5$ kJ/mol

13. $\Delta H_f\, HCl(g) = -92$ kJ/mol

$\Delta H_f\, Na_2SO_4(s) = -1382$ kJ/mol

$\Delta H_f\, H_2SO_4(l) = -811$ kJ/mol

$\Delta H_f\, NaCl(s) = -411$ kJ/mol

$\Delta rH = -2 \times 92 - 1382 + 811 + 2 \times 411 = 67$ kJ/mol

$\Delta H = \Delta U + \Delta ng\, RT$

$$67 = \Delta U + \frac{2 \times 8.3 \times 300}{1000} \Rightarrow \Delta U = 62.02 \text{ kJ/mol}$$

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14. $-16 = 2 - 2\ \Delta U_f^0\ NO_2(g)$

$\Delta U_f^0\ NO_2(g) = 9\ Kcal\ mol^{-1}$

$\frac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g)$

$\Delta n_g = -0.5$

15. $\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g)$

$\Delta rH = \frac{1}{2} \times 104 + \frac{1}{2} \times 58 - 103 = -22.0\ Kcal$

16. $ClF_3(g) \longrightarrow Cl(g) + 3F(g)$

$\Delta rH = 3 \in_{Cl-F} = 513\ kJ$

$\in_{Cl-F} = 171\ kJ$

17. $CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$

$\Delta rH = 4 \times \in_{C-H} + \in_{Cl-Cl} - 3 \times \in_{C-H} - 3 \times \in_{C-H} - \in_{C-Cl} - \in_{H-Cl}$

$-25 = x + y - 84 - 103$

$x + y = 162$ and $\frac{x}{y} = \frac{9}{5}$

$2.8\ y = 162 \quad x = 1.8\ y$

$\in_{Cl-Cl} = y = 57.75$

18. $Na^+(g) + I^-(g)$

$\Delta rH_2 = x_1 + \frac{x_2}{2} - 2x_3$

$\Delta rH_1 = x_1 + \frac{x_2}{2} - 2x_3 - x_4$

19. Form step-1 $\Delta rH = \in_{O-H}$

Form step-2 $\Delta rH = \in_{O-H}$

$2 \in_{O-H} = 498 + 428$

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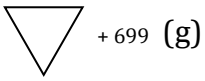
$\in_{O-H} = 463$ kJ/mol

20.  + 699 (g)

$\Delta rH = 3 \in_{C-C} - \in_{C-C} - \in_{C=C}$

$= 2 \in_{C-C} - \in_{C=C} = 2 \times 348 - 615 = +81$ kJ/mol

21. $5C(s) + 4H_2(g) \longrightarrow H_2C = C - C = CH_2(g)$

101 −390

$5C(s) + 4H_2(g) \longrightarrow H_2C = C - C = CH_2(g)$

$2 = 772 + \Delta H_{hyd}\ Na^+(g) + \Delta H_{hyd}\ Cl^-(g)$

$-770 = \Delta H_{hyd}\ Cl^-(g) + \frac{3}{2.5}\ \Delta H_{hyd}\ Cl^-(g)$

$\Delta H_{hyd}\ Cl^-(g) = \frac{-770 \times 2.5}{5.5} = -350$ kJ/mol

22. HCl (aq.) $\longrightarrow$ HCl (aq.) −2.5

4M 2M

1000 5 mole

HCl (aq.) $\longrightarrow$ HCl(aq.)

4M 2M

500 ml

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23. $CH_2 = CH_2 + H_2 \longrightarrow C_2H_6$

$\Delta rH = -132$ kJ/mol

$CH_2 = CH - CH = CH_2 + 2H_2 \xrightarrow{-255} C_3H_8$

$CH_2 = CH_2 + H_2 \longrightarrow C_2H_6$

$\Delta rH = -132$ kJ/mol

$CH_2 = CH - CH = CH_2 + 2H_2 \xrightarrow{-255} C_3H_8$

R.H. $\xrightarrow{-RE}$ 1.3 Butadiene $\xrightarrow{-2\times132}$ R.S

$\Delta rH = -140 - 115 = -255$

$-255 = -RE - 264 \Rightarrow RE = 255 - 264 = -9$ kJ

28. $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

$-57.3 = -285.8 - \Delta H_f^0\ OH^-(aq)$

$\Delta H_f^0\ OH^-(aq) = -285.8 + 57.3 = -228.5$ kJ/mol

29. Cp, m (B) = 300 J/mol

Cp, m (C) = 200 J/mol

Cp, m (A) = 150 J/mol

$(\Delta Cp)_r = 3 \times 200 - 150 - 2 \times 300 = -150$ J/mol

$$\Delta rH_{310K} + 10 = -\frac{150\times10}{1000}$$

$\Delta rH_{310K} = -10 - 1.5 = -11.5$ kJ/mol

30. $\Delta rG^\circ = \Delta G_f^0\ PCl_3(g) - \Delta G_f^0\ PCl_5(g)$

$= -60 + 74 = +14$ Kcal/mol

$\Delta_rG^\circ = -RT \ln k$

$$14 = -\frac{2\times1000}{1000} \ln k$$

$-7 = \ln k$

$-10 \ln 2 = \ln k \Rightarrow k = 2^{-10}$

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31. (i) $Au(OH)_3 + 4HCl \longrightarrow HAuCl_4 + 3H_2O$ $\Delta H = 28$ kcal

(ii) $Au(OH)_3 + 4HBr \longrightarrow HAuBr_4 + 3H_2O$ $\Delta H = -36.8$ kcal

(i) – (ii) = (iii)

(iii) $HAuBr_4 + 4HCl \longrightarrow HAuCl_4 + 4HBr$ $\Delta rH = 64.8$ kcal

$$\% \text{ conversion of } HAuBr_4 = \frac{0.44}{64.8} \times 100 = 0.6\ \%$$

33. C (graphite, s) $\longrightarrow$ C (diamond, s) $\Delta rH_1 = 1.9$ kJ

C (diamond, s) + $O_2(g) \longrightarrow CO_2(g)$ ΔrH_2

C (diamond, s) + $O_2(g) \longrightarrow CO_2(g)$ ΔrH_3

$\Delta rH_3 = \Delta rH_1 - \Delta rH_2$

C (diamond, s) $\longrightarrow$ C (graphite, s)