Hess's Law

69. Information given:

$$\begin{array}{rl} C(s) + O_2(g) \rightarrow CO_2(g) & \Delta H = -393.7\text{ kJ} \\ CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g) & \Delta H = -283.3\text{ kJ} \end{array}$$

Using Hess's law:

$$\begin{array}{rl} 2\ C(s) + 2\ O_2(g) \rightarrow 2\ CO_2(g) & \Delta H_1 = 2(-393.7\text{ kJ}) \\ 2\ CO_2(g) \rightarrow 2\ CO(g) + O_2(g) & \Delta H_2 = -2(-283.3\text{ kJ}) \\ \hline 2\ C(s) + O_2(g) \rightarrow 2\ CO(g) & \Delta H = \Delta H_1 + \Delta H_2 = -220.8\text{ kJ} \end{array}$$

Note: When an equation is reversed, the sign on ΔH is reversed. When the coefficients in a balanced equation are multiplied by an integer, then the value of ΔH is multiplied by the same integer.

70. Given:

$$\begin{array}{ll} C_4H_4(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l) & \Delta H_{comb} = -2341\text{ kJ} \\ C_4H_8(g) + 6\ O_2(g) \rightarrow 4\ CO_2(g) + 4\ H_2O(l) & \Delta H_{comb} = -2755\text{ kJ} \\ H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l) & \Delta H_{comb} = -286\text{ kJ} \end{array}$$

By convention, $H_2O(l)$ is produced when enthalpies of combustion are given, and because per-mole quantities are given, the combustion reaction refers to 1 mole of that quantity reacting with $O_2(g)$.

Using Hess's law to solve:

$$\begin{array}{rl} C_4H_4(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l) & \Delta H_1 = -2341\text{ kJ} \\ 4\ CO_2(g) + 4\ H_2O(l) \rightarrow C_4H_8(g) + 6\ O_2(g) & \Delta H_2 = -(-2755\text{ kJ}) \\ 2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) & \Delta H_3 = 2(-286\text{ kJ}) \\ \hline C_4H_4(g) + 2\ H_2(g) \rightarrow C_4H_8(g) & \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -158\text{ kJ} \end{array}$$

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71.

$$\begin{array}{rl} 2\ N_2(g) + 6\ H_2(g) \rightarrow 4\ NH_3(g) & \Delta H = -2(92\text{ kJ}) \\ 6\ H_2O(g) \rightarrow 6\ H_2(g) + 3\ O_2(g) & \Delta H = -3(-484\text{ kJ}) \\ \hline 2\ N_2(g) + 6\ H_2O(g) \rightarrow 3\ O_2(g) + 4\ NH_3(g) & \Delta H = 1268\text{ kJ} \end{array}$$

No, because the reaction is very endothermic (requires a lot of heat to react), it would not be a practical way of making ammonia because of the high energy costs required.

72.

$$\begin{array}{rl} \text{ClF} + 1/2\ O_2 \rightarrow 1/2\ Cl_2O + 1/2\ F_2O & \Delta H = 1/2(167.4\text{ kJ}) \\ 1/2\ Cl_2O + 3/2\ F_2O \rightarrow \text{ClF}_3 + O_2 & \Delta H = -1/2(341.4\text{ kJ}) \\ F_2 + 1/2\ O_2 \rightarrow F_2O & \Delta H = 1/2(-43.4\text{ kJ}) \\ \hline \underline{2}\ \text{ClF}(g) + \overset{2}{F_2}(g) \rightarrow \overset{2}{\text{ClF}_3} & \Delta H = -108.7\text{ kJ} \end{array}$$

73.

$$\begin{array}{rl} NO + O_3 \rightarrow NO_2 + O_2 & \Delta H = -199\text{ kJ} \\ 3/2\ O_2 \rightarrow O_3 & \Delta H = -1/2(-427\text{ kJ}) \\ O \rightarrow 1/2\ O_2 & \Delta H = -1/2(495\text{ kJ}) \\ \hline NO(g) + O(g) \rightarrow NO_2(g) & \Delta H = -233\text{ kJ} \end{array}$$

74. We want ΔH for $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(l)$. It will be easier to calculate ΔH for the combustion of four moles of N_2H_4 because we will avoid fractions.

$$\begin{array}{rl} 9\ H_2 + 9/2\ O_2 \rightarrow 9\ H_2O & \Delta H = 9(-286\text{ kJ}) \\ 3\ N_2H_4 + 3\ H_2O \rightarrow 3\ N_2O + 9\ H_2 & \Delta H = -3(-317\text{ kJ}) \\ 2\ NH_3 + 3\ N_2O \rightarrow 4\ N_2 + 3\ H_2O & \Delta H = -1010.\text{ kJ} \\ N_2H_4 + H_2O \rightarrow 2\ NH_3 + 1/2\ O_2 & \Delta H = -(-143\text{ kJ}) \\ \hline \underline{4}\ N_2H_4(l) + \underline{4}\ O_2(g) \rightarrow \underline{4}\ N_2(g) + \underline{8}\ H_2O(l) & \Delta H = -2490.\text{ kJ} \end{array}$$

$$\text{For } N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(l) \quad \Delta H = \frac{-2490.\text{ kJ}}{4} = -623\text{ kJ}$$

Note: By the significant figure rules, we could report this answer to four significant figures. However, because the ΔH values given in the problem are only known to ±1 kJ, our final answer will at best be ±1 kJ.

75.

$$\begin{array}{rl} CaC_2 \rightarrow \cancel{Ca} + 2\cancel{C} & \Delta H = -(-62.8\text{ kJ}) \\ \cancel{CaO} + H_2O \rightarrow Ca(OH)_2 & \Delta H = -653.1\text{ kJ} \\ 2\ \cancel{CO_2} + H_2O \rightarrow C_2H_2 + \cancel{5/2\ O_2} & \Delta H = -(-1300.\text{ kJ}) \\ \cancel{Ca} + \cancel{1/2\ O_2} \rightarrow \cancel{CaO} & \Delta H = -635.5\text{ kJ} \\ 2\ \cancel{C} + \cancel{2\ O_2} \rightarrow 2\ \cancel{CO_2} & \Delta H = 2(-393.5\text{ kJ}) \\ \hline CaC_2(s) + 2\ H_2O(l) \rightarrow Ca(OH)_2(aq) + C_2H_2(g) & \Delta H = -713\text{ kJ} \end{array}$$

76.

$P_4O_{10} \rightarrow P_4 + 5\ O_2$	$\Delta H = -(-2967.3\ kJ)$
$10\ PCl_3 + 5\ O_2 \rightarrow 10\ Cl_3PO$	$\Delta H = 10(-285.7\ kJ)$
$6\ PCl_5 \rightarrow 6\ PCl_3 + 6\ Cl_2$	$\Delta H = -6(-84.2\ kJ)$
$P_4 + 6\ Cl_2 \rightarrow 4\ PCl_3$	$\Delta H = -1225.6$
$P_4O_{10}(s) + 6\ PCl_5(g) \rightarrow 10\ Cl_3PO(g)$	$\Delta H = -610.1\ kJ$

Standard Enthalpies of Formation

77. The change in enthalpy that accompanies the formation of 1 mole of a compound from its elements, with all substances in their standard states, is the standard enthalpy of formation for a compound. The reactions that refer to ΔH_f° are:

$Na(s) + 1/2\ Cl_2(g) \rightarrow NaCl(s)$; $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

$6\ C(\text{graphite, s}) + 6\ H_2(g) + 3\ O_2(g) \rightarrow C_6H_{12}O_6(s)$

$Pb(s) + S(\text{rhombic, s}) + 2\ O_2(g) \rightarrow PbSO_4(s)$

78. a. Aluminum oxide = Al_2O_3; $2\ Al(s) + 3/2\ O_2(g) \rightarrow Al_2O_3(s)$

b. $C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$

c. $NaOH(aq) + HCl(aq) \rightarrow H_2O(l) + NaCl(aq)$

d. $2\ C(\text{graphite, s}) + 3/2\ H_2(g) + 1/2\ Cl_2(g) \rightarrow C_2H_3Cl(g)$

e. $C_6H_6(l) + 15/2\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(l)$

Note: ΔH_{comb} values assume 1 mole of compound combusted.

f. $NH_4Br(s) \rightarrow NH_4^+(aq) + Br^-(aq)$

79. In general, $\Delta H^\circ = \sum n_p \Delta H^\circ_{f,\text{ products}} - \sum n_r \Delta H^\circ_{f,\text{ reactants}}$, and all elements in their standard state have $\Delta H_f^\circ = 0$ by definition.

a. The balanced equation is $2\ NH_3(g) + 3\ O_2(g) + 2\ CH_4(g) \rightarrow 2\ HCN(g) + 6\ H_2O(g)$.

$$\Delta H^\circ = (2\ \text{mol HCN} \times \Delta H^\circ_{f,\text{HCN}} + 6\ \text{mol } H_2O(g) \times \Delta H^\circ_{f,H_2O})$$
$$- (2\ \text{mol } NH_3 \times \Delta H^\circ_{f,NH_3} + 2\ \text{mol } CH_4 \times \Delta H^\circ_{f,CH_4})$$

$$\Delta H^\circ = [2(135.1) + 6(-242)] - [2(-46) + 2(-75)] = -940.\ kJ$$

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b. $Ca_3(PO_4)_2(s) + 3\ H_2SO_4(l) \rightarrow 3\ CaSO_4(s) + 2\ H_3PO_4(l)$

$$\Delta H° = \left[3\ \text{mol}\ CaSO_4(s)\left(\frac{-1433\ \text{kJ}}{\text{mol}}\right) + 2\ \text{mol}\ H_3PO_4(l)\left(\frac{-1267\ \text{kJ}}{\text{mol}}\right)\right]$$

$$- \left[1\ \text{mol}\ Ca_3(PO_4)_2(s)\left(\frac{-4126\ \text{kJ}}{\text{mol}}\right) + 3\ \text{mol}\ H_2SO_4(l)\left(\frac{-814\ \text{kJ}}{\text{mol}}\right)\right]$$

$\Delta H° = -6833\ \text{kJ} - (-6568\ \text{kJ}) = -265\ \text{kJ}$

c. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

$$\Delta H° = (1\ \text{mol}\ NH_4Cl \times \Delta H°_{f,\,NH_4Cl}) - (1\ \text{mol}\ NH_3 \times \Delta H°_{f,\,NH_3} + 1\ \text{mol}\ HCl \times \Delta H°_{f,\,HCl})$$

$$\Delta H° = \left[1\ \text{mol}\left(\frac{-314\ \text{kJ}}{\text{mol}}\right)\right] - \left[1\ \text{mol}\left(\frac{-46\ \text{kJ}}{\text{mol}}\right) + 1\ \text{mol}\left(\frac{-92\ \text{kJ}}{\text{mol}}\right)\right]$$

$\Delta H° = -314\ \text{kJ} + 138\ \text{kJ} = -176\ \text{kJ}$

80. a. The balanced equation is $C_2H_5OH(l) + 3\ \cancel{O_2}(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g)$.

$$\Delta H° = \left[2\ \text{mol}\left(\frac{-393.5\ \text{kJ}}{\text{mol}}\right) + 3\ \text{mol}\left(\frac{-242\ \text{kJ}}{\text{mol}}\right)\right] - \left[1\ \text{mol}\left(\frac{-278\ \text{kJ}}{\text{mol}}\right)\right]$$

$\Delta H° = -1513\ \text{kJ} - (-278\ \text{kJ}) = -1235\ \text{kJ}$

b. $SiCl_4(l) + 2\ H_2O(l) \rightarrow SiO_2(s) + 4\ HCl(aq)$

Because HCl(aq) is $H^+(aq) + Cl^-(aq)$, $\Delta H°_f = 0 - 167 = -167$ kJ/mol.

$$\Delta H° = \left[4\ \text{mol}\left(\frac{-167\ \text{kJ}}{\text{mol}}\right) + 1\ \text{mol}\left(\frac{-911\ \text{kJ}}{\text{mol}}\right)\right] - \left[1\ \text{mol}\left(\frac{-687\ \text{kJ}}{\text{mol}}\right) + 2\ \text{mol}\left(\frac{-286\ \text{kJ}}{\text{mol}}\right)\right]$$

$\Delta H° = -1579\ \text{kJ} - (-1259\ \text{kJ}) = -320.\ \text{kJ}$

c. $MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s)$

$$\Delta H° = \left[1\ \text{mol}\left(\frac{-925\ \text{kJ}}{\text{mol}}\right)\right] - \left[1\ \text{mol}\left(\frac{-602\ \text{kJ}}{\text{mol}}\right) + 1\ \text{mol}\left(\frac{-286\ \text{kJ}}{\text{mol}}\right)\right]$$

$\Delta H° = -925\ \text{kJ} - (-888\ \text{kJ}) = -37\ \text{kJ}$

81. a. $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$; $\Delta H° = \sum n_p \Delta H°_{f,\,\text{products}} - \sum n_r \Delta H°_{f,\,\text{reactants}}$

$$\Delta H° = \left[4\ \text{mol}\left(\frac{90.\ \text{kJ}}{\text{mol}}\right) + 6\ \text{mol}\left(\frac{-242\ \text{kJ}}{\text{mol}}\right)\right] - \left[4\ \text{mol}\left(\frac{-46\ \text{kJ}}{\text{mol}}\right)\right] = -908\ \text{kJ}$$

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$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

$$\Delta H° = \left[2\text{ mol}\left(\frac{34\text{ kJ}}{\text{mol}}\right)\right] - \left[2\text{ mol}\left(\frac{90.\text{ kJ}}{\text{mol}}\right)\right] = -112\text{ kJ}$$

$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$

$$\Delta H° = \left[2\text{ mol}\left(\frac{-207\text{ kJ}}{\text{mol}}\right) + 1\text{ mol}\left(\frac{90.\text{ kJ}}{\text{mol}}\right)\right] - \left[3\text{ mol}\left(\frac{34\text{ kJ}}{\text{mol}}\right) + 1\text{ mol}\left(\frac{-286\text{ kJ}}{\text{mol}}\right)\right]$$

$$-140.\text{ kJ}$$

Note: All ΔH_f° values are assumed ±1 kJ.

b.

$$\begin{array}{l}
12\ NH_3(g) + 15\ O_2(g) \rightarrow 12\ NO(g) + 18\ H_2O(g) \\
12\ NO(g) + 6\ O_2(g) \rightarrow 12\ NO_2(g) \\
12\ NO_2(g) + 4\ H_2O(l) \rightarrow 8\ HNO_3(aq) + 4\ NO(g) \\
4\ H_2O(g) \rightarrow 4\ H_2O(l) \\
\hline
12\ NH_3(g) + 21\ O_2(g) \rightarrow 8\ HNO_3(aq) + 4\ NO(g) + 14\ H_2O(g)
\end{array}$$

The overall reaction is exothermic because each step is exothermic.

82. $4\ \cancel{Na}(s) + \cancel{O_2}(g) \rightarrow 2\ Na_2O(s) \quad \Delta H° = 2\text{ mol}\left(\frac{-416\text{ kJ}}{\text{mol}}\right) = -832\text{ kJ}$

$2\ \cancel{Na}(s) + 2\ H_2O(l) \rightarrow 2\ NaOH(aq) + \cancel{H_2}(g)$

$$\Delta H° = \left[2\text{ mol}\left(\frac{-470.\text{ kJ}}{\text{mol}}\right)\right] - \left[2\text{ mol}\left(\frac{-286\text{ kJ}}{\text{mol}}\right)\right] = -368\text{ kJ}$$

$2\cancel{Na}(s) + CO_2(g) \rightarrow Na_2O(s) + CO(g)$

$$\Delta H° = \left[1\text{ mol}\left(\frac{-416\text{ kJ}}{\text{mol}}\right) + 1\text{ mol}\left(\frac{-110.5\text{ kJ}}{\text{mol}}\right)\right] - \left[1\text{ mol}\left(\frac{-393.5\text{ kJ}}{\text{mol}}\right)\right] = -133\text{ kJ}$$

In Reactions 2 and 3, sodium metal reacts with the "extinguishing agent." Both reactions are exothermic, and each reaction produces a flammable gas, H_2 and CO, respectively.

83. $3\ Al(s) + 3\ NH_4ClO_4(s) \rightarrow Al_2O_3(s) + AlCl_3(s) + 3\ NO(g) + 6\ H_2O(g)$

$$\Delta H° = \left[6\text{ mol}\left(\frac{-242\text{ kJ}}{\text{mol}}\right) + 3\text{ mol}\left(\frac{90.\text{ kJ}}{\text{mol}}\right) + 1\text{ mol}\left(\frac{-704\text{ kJ}}{\text{mol}}\right) + 1\text{ mol}\left(\frac{-1676\text{ kJ}}{\text{mol}}\right)\right]$$

$$- \left[3\text{ mol}\left(\frac{-295\text{ kJ}}{\text{mol}}\right)\right] = -2677\text{ kJ}$$

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