Chapters 3 - Homework Solutions

3.1 n = 1.50 mol T = -23 °C + 273 = 250 K $\Delta_{vap}H^o$ = 26.0 kJ/mol

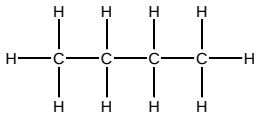
q = ΔH = n x $\Delta_{vap}H^o$ = 1.5 mol x 26.0 kJ/mol = 39.0 kJ

w = $-P_{exp}[V_g - V_l] \approx -PV_g = -nRT$ = -1.50 mol(8.314 J/mol-K)(250 K) = -3120 J = -3.1 kJ

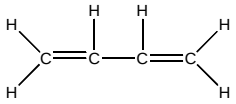
$\Delta U = q + w$ = 39.0 kJ - 3.1 kJ = 35.9 kJ

Note: Could have determined ΔU from $\Delta U = \Delta H - \Delta(PV)$

3.2 $C_4H_6(g) + 2\ H_2(g) \rightarrow C_4H_{10}(g)$ **n-butane**



1,3-butadiene



$$C_4H_6 + 2H_2 \xrightarrow{\Delta H_1} 4C + 10H \xrightarrow{\Delta H_2} C_4H_{10}$$

ΔH_1 = [2BE[C=C] + 1BE(C-C) + 6BE(CH-H)+ 2BE(H-H)
= [2(612) + 1(348) + 6(412) + 2(436] = +4916 kJ

ΔH_2 = -[3BE(C-C) + 10BE(C-H)
= -[3(348) + 10(412)] = -5164 kJ

$\Delta H = \Delta H_1 + \Delta H_2$ = +4916 - 5164 = -248 kJ

From Enthalpies of Formation, ΔH = -229 kJ (calc. val. is only 8% from experiment)

3.3 $C_6H_5C_2H_5(l) + (21/2)\ O_2(g) \rightarrow 8\ CO_2(g) + 5\ H_2O(l)$

$\Delta_cH^o = 8\ \Delta_fH^o(CO_2) + 5\ \Delta_fH^o(H_2O) - [1\ \Delta_fH^o(C_6H_5C_2H_5) + (21/2)\ \Delta_fH^o(O_2)]$

Δ_cH^o = 8(-393.5) + 5(-285.8) - [1(-12.5) + (21/2)(0)] = -4564.5 kJ

3.4 $3\ C(s) + 3\ H_2(g) + O_2(g) \rightarrow CH_3COOCH_3(l)$ $\Delta H = \Delta_fH^o$ = -442 kJ/mol

$\Delta U^o = \Delta H^o - \Delta(PV) = \Delta H^o - [n_{prod}(g)RT - n_{rct}(g)RT]$
$= \Delta H^o - RT[\Delta n(g)]$ = -442 kJ - (8.31 J/mol-K)(298 K)(-4 mol)
= -442 kJ + 9910 J = -442 kJ + 9.9 kJ = -432 kJ

3.5 $C_{10}H_8(s) + 12\ O_2(g) \rightarrow 10\ CO_2(g) + 4\ H_2O(l)$ $\Delta H = \Delta_c H^o = -5157$ kJ

$\Delta H = 10\ \Delta_f H^o(CO_2) + 4\ \Delta_f H^o(H_2O) - [1\ \Delta_f H^o(C_{10}H_8) + 12(0)]$

$-5157 = 10(-393.5) + 4(-285.8) - \Delta_f H^o(C_{10}H_8) \rightarrow \Delta_f H^o(C_{10}H_8) = +78.8$ kJ/mol $\approx +79$ kJ/mol

3.6 **(a)** In a constant volume (bomb) calorimeter, the heat directly equals the internal energy of combustion, $\Delta_c U^o$.

Therefore, $\Delta_c U^o = -1333$ kJ/mol. (negative because $q < 0$)

(b) HOOCCH═CHCOOH(s) + 3 $O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$

$\Delta n(g) = 4 - 3 = +1$ (note that you only count moles of **gas phase** molecules)

$\Delta_c H^o = \Delta_c U^o + \Delta n(g)RT = -1333$ kJ + (+1 mol)(8.314 J/mol-K)(298 K)

$= -1333$ kJ + 2500 J = -1333 kJ +2.5 kJ = -1330.5 kJ = -1331 kJ

(c) $\Delta_c H^o = 4\ \Delta_f H^o(CO_2) + 2\ \Delta_f H^o(H_2O) - [\Delta_f H^o(\text{Fum. Acid}) + 3(0)]$

$= 4(-393.5) + 2(-285.8) - \Delta_f H^o(\text{Fum. Acid}) = -1331$ kJ/mol

Therefore, $\Delta_f H^o(\text{Fum. Acid}) = -814.6 \approx 815$ kJ/mol

3.7
(a) exothermic, $\Delta H^o < 0$
(b) endothermic, $\Delta H^o > 0$
(c) endothermic, $\Delta H^o > 0$
(d) endothermic, $\Delta H^o > 0$
(e) endothermic, $\Delta H^o > 0$

3.8
(1) $2\ NO + O_2 \rightarrow 2\ NO_2$ $\Delta H_1 = -114.1$ kJ
(2) $4\ NO_2 + O_2 \rightarrow 2\ N_2O_5$ $\Delta H_2 = -110.2$ kJ
(3) $N_2 + O_2 \rightarrow 2\ NO$ $\Delta H_3 = +180.5$ kJ

(1') $2\ NO + O_2 \rightarrow 2\ NO_2$ $\Delta H_{1'} = -114.1$ kJ
(2') $2\ NO_2 + (1/2)\ O_2 \rightarrow N_2O_5$ $\Delta H_{2'} = (1/2)(-110.2\text{ kJ}) = -55.1$ kJ
(3') $N_2 + O_2 \rightarrow 2\ NO$ $\Delta H_{3'} = +180.5$ kJ

Add: $2\ NO + O_2 + 2\ NO_2 + (1/2)\ O_2 + N_2 + O_2 \rightarrow 2\ NO_2 + N_2O_5 + 2\ NO$

Simplifies to: $N_2 + (5/2)\ O_2 \rightarrow N_2O_5$ [Formation Reaction]

$\Delta H = \Delta_f H^o(N_2O_5) = \Delta H_{1'} + \Delta H_{2'} + \Delta H_{3'} = -114.1 - 55.1 + 180.5 = +11.3$ kJ

3.9 (1') $2\ N_2 + 2\ O_2 \rightarrow 4\ NO$ $\Delta H^{1'} = 2(180.7) = +361.4$ kJ

(2') $2\ N_2O \rightarrow 2\ N_2 + O_2$ $\Delta H^{2'} = -(1/2)(326.2) = -163.1$ kJ

Add: $2\ N_2O + O_2 \rightarrow 4\ NO$ $\Delta H = +361.4 - 163.1 = +198.3$ kJ

3.10 Reaction: $C_6H_6(l) + (15/2)\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(l)$

$$\Delta_{comb}H^o = 6\Delta_f H^o(CO_2) + 3\Delta_f H^o(H_2O) - 1\Delta_f H^o(C_6H_6) - 6 \cdot 0$$
$$= 6(-393.5) + 3(-285.8) - 1(49.0) = -3267.4\,kJ/mol$$
$$FV = -\frac{\Delta_{comb}H^o}{M} = -\frac{-3267.4\,kJ/mol}{78\,g/mol} = 41.9\,kJ/g$$

3.11 $$DV = -\frac{\Delta_{comb}H^o}{M} \rightarrow \Delta_{comb}H^o = -M \cdot DV$$
$$\Delta_{comb}H^o = -75\,g/mol \cdot 13.0\,kJ/g = -975\,kJ/mol$$

3.12

$$n(\mathrm{Pr}\,op) = \frac{210\,g}{60\,g/mol} = 3.5\,mol$$
$$\Delta H = n(\mathrm{Pr}\,op) \bullet \Delta_{comb}H(\mathrm{Pr}\,op)$$

$$\Delta_{comb}H^o(\mathrm{Pr}\,op) = \frac{\Delta H}{n(\mathrm{Pr}\,op)} = \frac{-7070\,kJ}{3.5\,mol} = -2020\,kJ/mol$$
$$FV = -\frac{-2020\,kJ/mol}{60\,g/mol} = +33.7\,kJ/g$$