CHAPTER 7

THERMOCHEMISTRY

PRACTICE EXAMPLES

1A **(E)** The heat absorbed is the product of the mass of water, its specific heat $(4.18 \text{ J g}^{-1}\,^{\circ}\text{C}^{-1})$, and the temperature change that occurs.

$$\text{heat energy} = 237 \text{ g} \times \frac{4.18 \text{ J}}{\text{g}\,^{\circ}\text{C}} \times (37.0\,^{\circ}\text{C} - 4.0\,^{\circ}\text{C}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 32.7 \text{ kJ of heat energy}$$

1B **(E)** The heat absorbed is the product of the amount of mercury, its molar heat capacity, and the temperature change that occurs.

$$\text{heat energy} = \left(2.50 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Hg}}{200.59 \text{ g Hg}}\right) \times \frac{28.0 \text{ J}}{\text{mol}\,^{\circ}\text{C}} \times \left[-6.0 - (-20.0)\right]^{\circ}\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$= 4.89 \text{ kJ of heat energy}$$

2A **(E)** First calculate the quantity of heat lost by the lead. This heat energy must be absorbed by the surroundings (water). We assume 100% efficiency in the energy transfer.

$$q_{\text{lead}} = 1.00 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{0.13 \text{ J}}{\text{g}\,^{\circ}\text{C}} \times (35.2\,^{\circ}\text{C} - 100.0\,^{\circ}\text{C}) = -8.4 \times 10^3 \text{ J} = -q_{\text{water}}$$

$$8.4 \times 10^3 \text{ J} = m_{\text{water}} \times \frac{4.18 \text{ J}}{\text{g}\,^{\circ}\text{C}} \times (35.2\,^{\circ}\text{C} - 28.5\,^{\circ}\text{C}) = 28 m_{\text{water}} \qquad m_{\text{water}} = \frac{8.4 \times 10^3 \text{ J}}{28 \text{ J g}^{-1}} = 3.0 \times 10^2 \text{ g}$$

2B **(M)** We use the same equation, equating the heat lost by the copper to the heat absorbed by the water, except now we solve for final temperature.

$$q_{\text{Cu}} = 100.0 \text{ g} \times \frac{0.385 \text{ J}}{\text{g}\,^{\circ}\text{C}} \times (x\,^{\circ}\text{C} - 100.0\,^{\circ}\text{C}) = -50.0 \text{ g} \times \frac{4.18 \text{ J}}{\text{g}\,^{\circ}\text{C}} \times (x\,^{\circ}\text{C} - 26.5\,^{\circ}\text{C}) = -q_{\text{water}}$$

$$38.5x - 3850 = -209x + 5539 \text{ J} \qquad 38.5x + 209x = 5539 + 3850 \rightarrow 247.5x = 9389$$

$$x = \frac{9389 \text{ J}}{247.5 \text{ J }^{\circ}\text{C}^{-1}} = 37.9\,^{\circ}\text{C}$$

3A **(E)** The molar mass of $C_8H_8O_3$ is 152.15 g/mol. The calorimeter has a heat capacity of $4.90 \text{ kJ}/^{\circ}\text{C}$.

$$q_{\text{calor}} = \frac{4.90 \text{ kJ}\,^{\circ}\text{C}^{-1} \times (30.09\,^{\circ}\text{C} - 24.89\,^{\circ}\text{C})}{1.013 \text{ g}} \times \frac{152.15 \text{ g}}{1 \text{ mol}} = 3.83 \times 10^3 \text{ kJ / mol}$$

$$\Delta H_{\text{comb}} = -q_{\text{calor}} = -3.83 \times 10^3 \text{ kJ / mol}$$

3B **(E)** The heat that is liberated by the benzoic acid's combustion serves to raise the temperature of the assembly. We designate the calorimeter's heat capacity by C.

$$q_{rxn} = 1.176 \text{ g} \times \frac{-26.42 \text{ kJ}}{1 \text{ g}} = -31.07 \text{ kJ} = -q_{calorim}$$

$$q_{calorim} = C\Delta t = 31.07 \text{ kJ} = C \times 4.96°C \qquad C = \frac{31.07 \text{ kJ}}{4.96°C} = 6.26 \text{ kJ} /° C$$

4A **(M)** The heat that is liberated by the reaction raises the temperature of the reaction mixture. We assume that this reaction mixture has the same density and specific heat as pure water.

$$q_{calorim} = \left(200.0 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}}\right) \times \frac{4.18 \text{ J}}{\text{g}°C} \times (30.2 - 22.4)°C = 6.5 \times 10^3 \text{ J} = -q_{rxn}$$

Owing to the 1:1 stoichiometry of the reaction, the number of moles of AgCl(s) formed is equal to the number of moles of AgNO₃(aq) in the original sample.

$$\text{moles AgCl} = 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.00 \text{ M AgNO}_3}{1 \text{ L}} \times \frac{1 \text{ mol AgCl}}{1 \text{ mol AgNO}_3} = 0.100 \text{ mol AgCl}$$

$$q_{rxn} = \frac{-6.5 \times 10^3 \text{ J}}{0.100 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -65. \text{ kJ/mol}$$

Because q_{rxn} is a negative quantity, the precipitation reaction is exothermic.

4B **(M)** The assumptions include no heat loss to the surroundings or to the calorimeter, a solution density of 1.00 g/mL, a specific heat of $4.18 \text{ J g}^{-1}°C^{-1}$, and that the initial and final solution volumes are the same. The equation for the reaction that occurs is $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$. Since the two reactants combine in a one to one mole ratio, the limiting reactant is the one present in smaller amount (i.e. the one with a smaller molar quantity).

$$\text{amount HCl} = 100.0 \text{ mL} \times \frac{1.020 \text{ mmol HCl}}{1 \text{ mL soln}} = 102.0 \text{ mmol HCl}$$

$$\text{amount NaOH} = 50.0 \text{ mL} \times \frac{1.988 \text{ mmol NaOH}}{1 \text{ mL soln}} = 99.4 \text{ mmol NaOH}$$

Thus, NaOH is the limiting reactant.

$$q_{neutr} = 99.4 \text{ mmol NaOH} \times \frac{1 \text{ mmol H}_2O}{1 \text{ mmol NaOH}} \times \frac{1 \text{ mol H}_2O}{1000 \text{ mmol H}_2O} \times \frac{-56 \text{ kJ}}{1 \text{ mol H}_2O} = -5.57 \text{ kJ}$$

$$q_{calorim} = -q_{neutr} = 5.57 \text{ kJ} = (100.0 + 50.0) \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{4.18 \text{ J}}{\text{g}°C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times (t - 24.52°C)$$

$$= 0.627t - 15.37 \qquad t = \frac{5.57 + 15.37}{0.627} = 33.4°C$$

5A **(E)** $w = -P\Delta V = -0.750 \text{ atm}(+1.50 \text{ L}) = -1.12\underline{5} \text{ L atm} \times \frac{101.33 \text{ J}}{1 \text{ L atm}} = -114 \text{ J}$

114 J of work is done by system

5B **(M)** Determine the initial number of moles:

$$n = 50.0 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.014 \text{ g N}_2} = 1.78\underline{5} \text{ moles of N}_2$$

$$V = \frac{nRT}{P} = \frac{(1.785 \text{ mol N}_2)(0.08206 \text{ Latm K}^{-1}\text{mol}^{-1})(293.15 \text{ K})}{2.50 \text{ atm}} = 17.2 \text{ L}$$

$$\Delta V = 17.2 - 75.0 \text{ L} = -57.8 \text{ L}$$

$$w = -P\Delta V = -2.50 \text{ atm}(-57.8 \text{ L}) \times \frac{101.33 \text{ J}}{1 \text{ L atm}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = +14.6 \text{ kJ} \text{ work done on system.}$$

6A **(E)** The work is $w = +355$ J. The heat flow is $q = -185$ J. These two are related to the energy change of the system by the first law equation: $\Delta U = q + w$, which becomes

$$\Delta U = +355 \text{ J} - 185 \text{ J} = +1.70 \times 10^2 \text{ J}$$

6B **(E)** The internal energy change is $\Delta U = -125$ J. The heat flow is $q = +54$ J. These two are related to the work done on the system by the first law equation: $\Delta U = q + w$, which becomes $-125 \text{ J} = +54 \text{ J} + w$. The solution to this equation is $w = -125 \text{ J} - 54 \text{ J} = -179 \text{ J}$, which means that 179 J of work is done by the system to the surroundings.

7A **(E)** Heat that is given off has a negative sign. In addition, we use the molar mass of sucrose, 342.30 g/mol.

$$\text{sucrose mass} = -1.00 \times 10^3 \text{ kJ} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{-5.65 \times 10^3 \text{ kJ}} \times \frac{342.30 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} = 60.6 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}$$

7B **(E)** Although the equation does not say so explicitly, the reaction of $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ gives off 56 kJ of heat per mole of water formed. The equation then is the source of a conversion factor.

$$\text{heat flow} = 25.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1045 \text{ mol HCl}}{1 \text{ L soln}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol HCl}} \times \frac{56 \text{ kJ evolved}}{1 \text{ mol H}_2\text{O}}$$

heat flow = 0.15 kJ heat evolved

8A **(M)** $V_{ice} = (2.00 \text{ cm})^3 = 8.00 \text{ cm}^3$

$$m_{ice} = m_{water} = 8.00 \text{ cm}^3 \times 0.917 \text{ g cm}^{-3} = 7.34 \text{ g ice} = 7.34 \text{ g H}_2\text{O}$$

$$\text{moles of ice} = 7.34 \text{ g ice} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 0.407 \text{ moles of ice}$$

$$q_{overall} = q_{ice}(-10 \text{ to } 0 \text{ °C}) + q_{fus} + q_{water}(0 \text{ to } 23.2 \text{ °C})$$

$$q_{overall} = m_{ice}(\text{sp. ht.})_{ice}\Delta T + n_{ice}\Delta H_{fus} + m_{water}(\text{sp. ht.})_{water}\Delta T$$

$$q_{overall} = 7.34 \text{ g}(10.0 \text{ °C})(2.01 \frac{\text{J}}{\text{g °C}}) + 0.407 \text{ mol ice}(6.01 \frac{\text{kJ}}{\text{mol}}) + 7.34 \text{ g}(23.2 \text{ °C})(4.184 \frac{\text{J}}{\text{g °C}})$$

$$q_{overall} = 0.148 \text{ kJ} + 2.45 \text{ kJ} + 0.712 \text{ kJ}$$

$$q_{overall} = +3.31 \text{ kJ (the system absorbs this much heat)}$$

8B **(M)** 5.00×10^3 kJ = q_{ice}(−15 to 0 °C) + q_{fus} + q_{water} (0 to 25 °C)+ q_{vap}

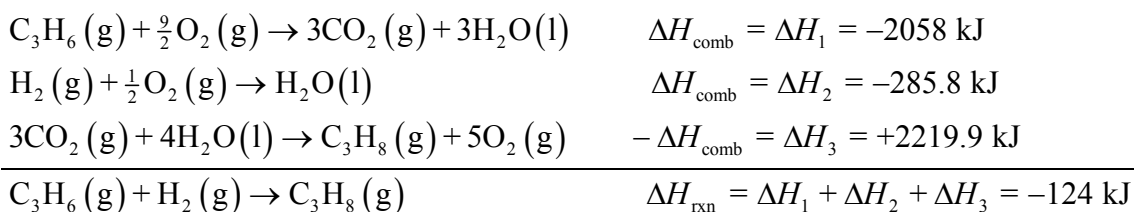5.00×10^3 kJ = m_{ice}(sp. ht.)$_{ice}\Delta T$ + $n_{ice}\Delta H_{fus}$ + m_{water}(sp. ht.)$_{water}\Delta T$ + $n_{water}\Delta H_{vap}$

$$5.00 \times 10^6 \text{ J} = m(15.0 °C)(2.01 \frac{\text{J}}{\text{g °C}}) + (\frac{m}{18.015 \text{ g H}_2\text{O/mol H}_2\text{O}} \times 6.01 \times 10^3 \frac{\text{J}}{\text{mol}})$$

$$+ m(25.0 °C)(4.184 \frac{\text{J}}{\text{g °C}}) + \frac{m}{18.015 \text{ g H}_2\text{O/mol}}(44.0 \times 10^3 \frac{\text{J}}{\text{mol}})$$

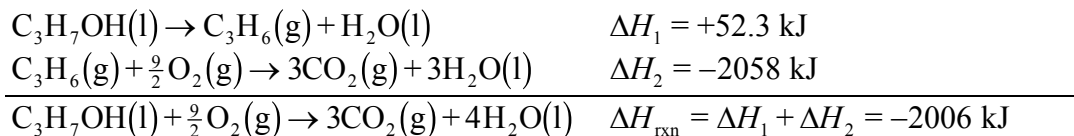5.00×10^6 J = m(30.1$\underline{5}$ J/g) + m(333.$\underline{6}$ J/g) + m(104.$\underline{5}$ J/g) + m(2.4$\underline{4} \times 10^3$ J/g)

5.00×10^6 J = m(2.91 $\times 10^3$ J/g) $m = \dfrac{5.00 \times 10^6 \text{ J}}{2.91 \times 10^3 \text{ J/g}}$ = 1718 g or 1.72 kg H_2O

**9A** **(M)** We combine the three combustion reactions to produce the hydrogenation reaction.

$C_3H_6(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$ $\Delta H_{comb} = \Delta H_1 = -2058$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H_{comb} = \Delta H_2 = -285.8$ kJ

$3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g)$ $-\Delta H_{comb} = \Delta H_3 = +2219.9$ kJ

$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$ $\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 = -124$ kJ

9B **(M)** The combustion reaction has propanol and $O_{2(g)}$ as reactants; the products are $CO_2(g)$ and $H_2O(l)$. Reverse the reaction given and combine it with the combustion reaction of $C_3H_6(g)$.

$C_3H_7OH(l) \rightarrow C_3H_6(g) + H_2O(l)$ $\Delta H_1 = +52.3$ kJ

$C_3H_6(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$ $\Delta H_2 = -2058$ kJ

$C_3H_7OH(l) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H_{rxn} = \Delta H_1 + \Delta H_2 = -2006$ kJ

10A **(M)** The enthalpy of formation is the enthalpy change for the reaction in which one mole of the product, $C_6H_{13}O_2N(s)$, is produced from appropriate amounts of the reference forms of the elements (in most cases, the most stable form of the elements).

$6 \text{ C(graphite)} + \frac{13}{2}H_2(g) + O_2(g) + \frac{1}{2}N_2(g) \rightarrow C_6H_{13}O_2N(s)$
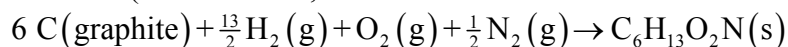
10B **(M)** The enthalpy of formation is the enthalpy change for the reaction in which one mole of the product, $NH_3(g)$, is produced from appropriate amounts of the reference forms of the elements, in this case from 0.5 mol $N_2(g)$ and 1.5 mol $H_2(g)$, that is, for the reaction:

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$
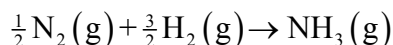
The specified reaction is twice the reverse of the formation reaction, and its enthalpy change is minus two times the enthalpy of formation of $NH_3(g)$:

$-2 \times (-46.11 \text{ kJ}) = +92.22$ kJ

11A **(M)** $\Delta H^{\circ}_{rxn}=2\times\Delta H^{\circ}_{f}\left[CO_2\left(g\right)\right]+3\times\Delta H^{\circ}_{f}\left[H_2O\left(l\right)\right]-\Delta H^{\circ}_{f}\left[CH_3CH_2OH\left(l\right)\right]-3\times\Delta H^{\circ}_{f}\left[O_2\left(g\right)\right]$

$$=\left[2\times\left(-393.5\ kJ\right)\right]+\left[3\times\left(-285.8\ kJ\right)\right]-\left[-277.7\ kJ\right]-\left[3\times0.00\ kJ\right]=-1367\ kJ$$

11B **(D)** We write the combustion reaction for each compound, and use that reaction to determine the compound's heat of combustion.

$$C_3H_8\left(g\right)+5O_2\left(g\right)\rightarrow3CO_2\left(g\right)+4H_2O\left(l\right)$$
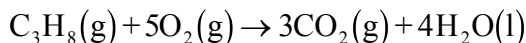
$\Delta H^{\circ}_{combustion}=3\times\Delta H^{\circ}_{f}\left[CO_2\left(g\right)\right]+4\times\Delta H^{\circ}_{f}\left[H_2O\left(l\right)\right]-\Delta H^{\circ}_{f}\left[C_3H_8\left(g\right)\right]-5\times\Delta H^{\circ}_{f}\left[O_2\left(g\right)\right]$

$$=\left[3\times\left(-393.5\ kJ\right)\right]+\left[4\times\left(-285.8\ kJ\right)\right]-\left[-103.8\ kJ\right]-\left[5\times0.00\ kJ\right]$$

$$=-1181\ kJ-1143\ kJ+103.8-0.00\ kJ\ =\ -2220.\ kJ/mol\ C_3H_8$$

$$C_4H_{10}\left(g\right)+\tfrac{13}{2}O_2\left(g\right)\rightarrow4CO_2\left(g\right)+5H_2O\left(l\right)$$
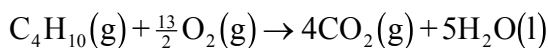
$\Delta H^{\circ}_{combustion}=4\times\Delta H^{\circ}_{f}\left[CO_2\left(g\right)\right]+5\times\Delta H^{\circ}_{f}\left[H_2O\left(l\right)\right]-\Delta H^{\circ}_{f}\left[C_4H_{10}\left(g\right)\right]-6.5\times\Delta H^{\circ}_{f}\left[O_2\left(g\right)\right]$

$$=\left[4\times\left(-393.5\ kJ\right)\right]+\left[5\times\left(-285.8\ kJ\right)\right]-\left[-125.6\right]-\left[6.5\times0.00\ kJ\right]$$

$$=-1574\ kJ-1429\ kJ+125.6\ kJ-0.00K\ kJ=-2877\ kJ/mol\ C_4H_{10}$$

In 1.00 mole of the mixture there are 0.62 mol $C_3H_8\left(g\right)$ and 0.38 mol $C_4H_{10}\left(g\right)$.

$$\text{heat of combustion}=\left(0.62\ mol\ C_3H_8\times\frac{-2220.\ kJ}{1\ mol\ C_3H_8}\right)+\left(0.38\ mol\ C_4H_{10}\times\frac{-2877\ kJ}{1\ mol\ C_4H_{10}}\right)$$

$$=-1.4\times10^3\ kJ-1.1\times10^3\ kJ=-2.5\times10^3\ kJ/\text{mole of mixture}$$

12A **(M)** $6\ CO_2(g)+6\ H_2O(l)\rightarrow\ C_6H_{12}O_6(s)+6\ O_2(g)$
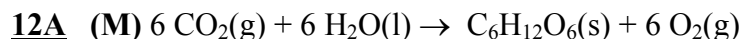
$\Delta H^{\circ}_{rxn}=2803\ kJ=\Sigma\ \Delta H^{\circ}_{f\ products}-\Sigma\ \Delta H^{\circ}_{f\ reactants}$

$2803\ kJ=[1\ mol(\Delta H^{\circ}_{f}\ [C_6H_{12}O_6(s)])+6\ mol(0\frac{kJ}{mol})]-[6\ mol(-393.5\frac{kJ}{mol})+6\ mol\ (-285.8\frac{kJ}{mol})]$

$2803\ kJ=\ \Delta H^{\circ}_{f}\ [C_6H_{12}O_6(s)]-[-4075.8\ kJ].$ Thus, $\Delta H^{\circ}_{f}\ [C_6H_{12}O_6(s)]=-1273\ kJ/mol\ C_6H_{12}O_6(s)$

12B **(M)** $\Delta H^{\circ}_{comb}[CH_3OCH_3(g)]=-31.70\ \dfrac{kJ}{g}$ molar mass of $CH_3OCH_3=46.069$ g mol^{-1}

$\Delta H^{\circ}_{comb}[CH_3OCH_3(g)]=-31.70\ \dfrac{kJ}{g}\times46.069\ \dfrac{g}{mol}=-1460\ \dfrac{kJ}{mol}\ kJ=\Delta H^{\circ}_{rxn}$

$\Delta H^{\circ}_{rxn}=\Sigma\ \Delta H^{\circ}_{f\ products}-\Sigma\ \Delta H^{\circ}_{f\ reactants}$ Reaction: $CH_3OCH_3(g)+3\ O_2(g)\rightarrow\ 2\ CO_2(g)+3\ H_2O(l)$

$-1460\ kJ=[2\ mol(-393.5\frac{kJ}{mol})+3\ mol\ (-285.8\ \frac{kJ}{mol})]-[1\ mol(\Delta H^{\circ}_{f}\ [CH_3OCH_3(g)])+3\ mol(0\frac{kJ}{mol})]$

$-1460\ kJ=-1644.4\ kJ-\Delta H^{\circ}_{f}\ [CH_3OCH_3(g)]$

Hence, $\Delta H^{\circ}_{f}\ [CH_3OCH_3(g)]=-184\ kJ/mol\ CH_3OCH_3(g)$

13A **(M)** The net ionic equation is: $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$ and we have the following:

$$\Delta H^\circ_{rxn} = \Delta H^\circ_f\left[AgI(s)\right] - \left[\Delta H^\circ_f\left[Ag^+(aq)\right] + \Delta H^\circ_f\left[I^-(aq)\right]\right]$$

$$= -61.84 \text{ kJ/mol} - \left[(+105.6 \text{ kJ/mol}) + (-55.19 \text{ kJ/mol})\right] = -112.3 \text{ kJ/mol AgI(s) formed}$$

13B **(M)** $2 Ag^+(aq) + CO_3^{2-}(aq) \rightarrow Ag_2CO_3(s)$

$\Delta H^\circ_{rxn} = -39.9 \text{ kJ} = \Sigma \Delta H^o_f \text{ products} - \Sigma \Delta H^o_f \text{ reactants} =$

$-39.9 \text{ kJ} = \Delta H^o_f [Ag_2CO_3(s)] - [2 \text{ mol}(105.6 \dfrac{\text{kJ}}{\text{mol}}) + 1 \text{ mol}(-677.1 \dfrac{\text{kJ}}{\text{mol}})]$

$-39.9 \text{ kJ} = \Delta H^o_f [Ag_2CO_3(s)] + 465.9 \text{ kJ}$

Hence, $\Delta H^o_f [Ag_2CO_3(s)] = -505.8 \text{ kJ/mol Ag}_2CO_3(s)$ formed.

INTEGRATIVE EXAMPLE

A. (M) The combustion reactions of $C_{16}H_{32}$ and $C_{16}H_{34}$ are shown below

(1) $C_{16}H_{32} + 24 O_2 \rightarrow 16 CO_2 + 16 H_2O$ $\Delta H_f = -10539 \text{ kJ}$
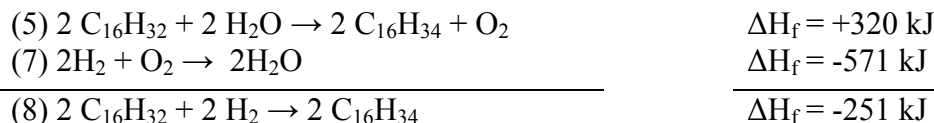(2) $2 C_{16}H_{34} + 49 O_2 \rightarrow 32 CO_2 + 34 H_2O$ $\Delta H_f = -10699 \text{ kJ/mol} = -21398 \text{ kJ}$

Since we are studying the hydrogenation of $C_{16}H_{32}$ to give $C_{16}H_{34}$, the final equation has to include the former as the reactant and the latter as the product. This is done by doubling equation 1 and reversing equation 2:

(3) $2 C_{16}H_{32} + 48 O_2 \rightarrow 32 CO_2 + 32 H_2O$ $\Delta H_f = -21078 \text{ kJ}$
(4) $32 CO_2 + 34 H_2O \rightarrow 2 C_{16}H_{34} + 49 O_2$ $\Delta H_f = +21398 \text{ kJ}$
(5) $2 C_{16}H_{32} + 2 H_2O \rightarrow 2 C_{16}H_{34} + O_2$ $\Delta H_f = +320 \text{ kJ}$
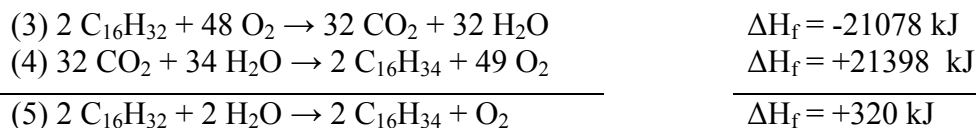
Since a hydrogenation reaction involves hydrogen as a reactant, and looking at equation (5), we add the following reaction to (5):

(6) $H_2 + ½ O_2 \rightarrow H_2O$ $\Delta H_f = -285.5 \text{ kJ/mol}$

Double equation (6) and add it to equation 5:

(5) $2 C_{16}H_{32} + 2 H_2O \rightarrow 2 C_{16}H_{34} + O_2$ $\Delta H_f = +320 \text{ kJ}$
(7) $2H_2 + O_2 \rightarrow 2H_2O$ $\Delta H_f = -571 \text{ kJ}$
(8) $2 C_{16}H_{32} + 2 H_2 \rightarrow 2 C_{16}H_{34}$ $\Delta H_f = -251 \text{ kJ}$

Since (8) is for 2 moles, ΔH_f is -125.5 kJ/mol

B. (D) This is a multi-stage problem. First, you must determine the amount of material reacted, then you have to determine the amount of heat generated, and then you have to calculate the effect of that heat on water evaporation:
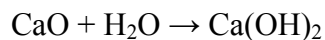
$$CaO + H_2O \rightarrow Ca(OH)_2$$

56 g CaO × (1 mol CaO/56.0 g CaO) = 1 mol CaO
100 g H_2O × (1 mol H_2O/18.0 g H_2O) = 5.56 mol H_2O

CaO is the limiting reagent. Therefore, amount of unreacted H_2O is = 5.56 − 1.0 = 4.56 mol
The mass of water unreacted = 82.0 g H_2O

$$56 \text{ g CaO} \times \frac{1 \text{ mol CaO}}{56.0 \text{ g CaO}} \times \frac{1 \text{ mol Ca(OH)}_2}{1 \text{ mol CaO}} \times \frac{74.12 \text{ g Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2} = 74.1 \text{ g Ca(OH)}_2$$

$$\Delta H^\circ_{rxn} = H^\circ_f\left(Ca(OH)_2 \times mol\right) - \left(H^\circ_f\left(CaO\right) \times mol + H^\circ_f\left(H_2O\right) \times mol\right)$$

$$\Delta H^\circ_{rxn} = -987 \text{ kJ/mol} \times 1 \text{ mol} - \left(-635 \text{ kJ/mol} \times 1 \text{ mol} + \left(-286 \text{ kJ/mol} \times 1 \text{ mol}\right)\right) = -66 \text{ kJ}$$

As stated before, we have to determine the effects of the heat on the water in the reaction. The water first needs to be heated to 100 °C, and then evaporated. The energy needed to heat 82.0 g of the water remaining in the reaction is:
$$J = -m \cdot c \cdot \Delta T = -(82.0 \text{ g})\left(4.187 \text{J} \cdot \text{g}^{-1} {}^\circ\text{C}^{-1}\right)\left(100°C - 20°C\right) = -27.47 \text{ kJ}$$

Therefore, 27.47 kJ of energy is used up for the water in the reaction to go from 20 to 100 °C. The energy remaining is -66 − (-27.47) = 38.53 kJ.

Since ΔH_{vap} of water is 44.06 kJ/mol, we can calculate the amount of water evaporated:
$$38.53 \text{ kJ} \times \frac{1 \text{ mol H}_2O}{44.06 \text{ kJ}} \times \frac{18 \text{ g H}_2O}{1 \text{ mol H}_2O} = 15.74 \text{ g H}_2O \text{ evaporated}$$

Based on the above, the contents of the vessel after completion of the reaction are 74.1 g of $Ca(OH)_2$ and 66.3 g of H_2O.

EXERCISES

Heat Capacity (Specific Heat)

1. **(E)**

   (a) $q = 9.25 \text{ L} \times \dfrac{1000 \text{ cm}^3}{1 \text{ L}} \times \dfrac{1.00 \text{ g}}{1 \text{ cm}^3} \times \dfrac{4.18 \text{ J}}{1 \text{ g}\,^{\circ}\text{C}} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}} \left(29.4\,^{\circ}\text{C} - 22.0\,^{\circ}\text{C}\right) = +2.9 \times 10^2 \text{ kJ}$

   (b) $q = 5.85 \text{ kg} \times \dfrac{1000 \text{ g}}{1 \text{ kg}} \times \dfrac{0.903 \text{ J}}{\text{g}\,^{\circ}\text{C}} \times \left(-33.5\,^{\circ}\text{C}\right) \times \dfrac{1 \text{ kJ}}{1000 \text{ J}} = -177 \text{ kJ}$

2. **(E)** $\text{heat} = \text{mass} \times \text{sp ht} \times \Delta T$

   (a) $\Delta T = \dfrac{+875 \text{ J}}{12.6 \text{ g} \times 4.18 \text{ J g}^{-1}\,^{\circ}\text{C}^{-1}} = +16.6\,^{\circ}\text{C}$ $T_f = T_i + \Delta T = 22.9\,^{\circ}\text{C} + 16.6\,^{\circ}\text{C} = 39.5\,^{\circ}\text{C}$

   (b) $\Delta T = \dfrac{-1.05 \text{ kcal} \times \dfrac{1000 \text{ cal}}{1 \text{ kcal}}}{\left(1.59 \text{ kg} \times \dfrac{1000 \text{ g}}{1 \text{ kg}}\right) 0.032 \dfrac{\text{cal}}{\text{g}\,^{\circ}\text{C}}} = -21\,^{\circ}\text{C}$ $T_f = T_i + \Delta T = 22.9\,^{\circ}\text{C} - 21.0\,^{\circ}\text{C} = 8.9\,^{\circ}\text{C}$

3. **(E)** heat gained by the water $=$ heat lost by the metal; $\text{heat} = \text{mass} \times \text{sp.ht.} \times \Delta T$

   (a) $50.0 \text{ g} \times 4.18 \dfrac{\text{J}}{\text{g}\,^{\circ}\text{C}} \left(38.9 - 22.0\right)\,^{\circ}\text{C} = 3.53 \times 10^3 \text{ J} = -150.0\text{g} \times \text{sp.ht.} \times \left(38.9 - 100.0\right)\,^{\circ}\text{C}$

      $\text{sp.ht.} = \dfrac{3.53 \times 10^3 \text{ J}}{150.0 \text{ g} \times 61.1\,^{\circ}\text{C}} = 0.385 \text{ J g}^{-1}\,^{\circ}\text{C}^{-1} \text{ for Zn}$

   (b) $50.0 \text{ g} \times 4.18 \dfrac{\text{J}}{\text{g}\,^{\circ}\text{C}} \left(28.8 - 22.0\right)\,^{\circ}\text{C} = 1.4 \times 10^3 \text{ J} = -150.0\text{g} \times \text{sp.ht.} \times \left(28.8 - 100.0\right)\,^{\circ}\text{C}$

      $\text{sp.ht.} = \dfrac{1.4 \times 10^3 \text{ J}}{150.0 \text{ g} \times 71.2\,^{\circ}\text{C}} = 0.13 \text{ J g}^{-1}\,^{\circ}\text{C}^{-1} \text{ for Pt}$

   (c) $50.0 \text{ g} \times 4.18 \dfrac{\text{J}}{\text{g}\,^{\circ}\text{C}} \left(52.7 - 22.0\right)\,^{\circ}\text{C} = 6.42 \times 10^3 \text{ J} = -150.0\text{g} \times \text{sp.ht.} \times \left(52.7 - 100.0\right)\,^{\circ}\text{C}$

      $\text{sp.ht.} = \dfrac{6.42 \times 10^3 \text{ J}}{150.0 \text{ g} \times 47.3\,^{\circ}\text{C}} = 0.905 \text{ J g}^{-1}\,^{\circ}\text{C}^{-1} \text{ for Al}$

4. **(E)** $50.0 \text{ g} \times 4.18 \dfrac{\text{J}}{\text{g}\,^{\circ}\text{C}} \left(27.6 - 23.2\right)\,^{\circ}\text{C} = 9.2 \times 10^2 \text{ J} = -75.0 \text{ g} \times \text{sp.ht.} \times \left(27.6 - 80.0\right)\,^{\circ}\text{C}$

$\text{sp.ht.} = \dfrac{9.2 \times 10^2 \text{ J}}{75.0 \text{ g} \times 52.4\,^{\circ}\text{C}} = 0.23 \text{ J g}^{-1}\,^{\circ}\text{C}^{-1} \text{ for Ag}$

5. **(M)** $q_{\text{water}} = 375 \text{ g} \times 4.18 \dfrac{\text{J}}{\text{g}\,^{\circ}\text{C}} \left(87 - 26\right)\,^{\circ}\text{C} = 9.5\underline{6} \times 10^4 \text{ J} = -q_{\text{iron}}$

$q_{\text{iron}} = -9.5\underline{6} \times 10^4 \text{ J} = 465 \text{g} \times 0.449 \dfrac{\text{J}}{\text{g}\,^{\circ}\text{C}} \left(87 - T_l\right) = 1.81\underline{6} \times 10^4 \text{J} - 2.08\underline{8} \times 10^2 \, T_l$

$$T_l = \frac{-9.56 \times 10^4 - 1.816 \times 10^4}{-2.088 \times 10^2} = \frac{-11.38 \times 10^4}{-2.088 \times 10^2} = 5.448 \times 10^2 \,^{\circ}C \text{ or } 545 \,^{\circ}C$$

The number of significant figures in the final answer is limited by the two significant figures for the given temperatures.

6. **(M)** heat lost by steel = heat gained by water

$$-m \times 0.50 \frac{J}{g\,^{\circ}C}(51.5 - 183)\,^{\circ}C = 66\, m = 125 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times 4.18 \frac{J}{g\,^{\circ}C}(51.5 - 23.2)\,^{\circ}C$$

$$66\, m = 1.48 \times 10^4 \text{ J} \qquad m = \frac{1.48 \times 10^4}{66} = 2.2 \times 10^2 \text{ g stainless steel.}$$

The precision of this method of determining mass is limited by the fact that some heat leaks out of the system. When we deal with temperatures far above (or far below) room temperature, this assumption becomes less and less valid. Furthermore, the precision of the method is limited to two significant figures by the specific heat of the steel. If the two specific heats were known more precisely, then the temperature difference would determine the final precision of the method. It is unlikely that we could readily measure temperatures more precisely than $\pm 0.01\,^{\circ}C$, without expensive equipment. The mass of steel in this case would be measurable to four significant figures, to ± 0.1 g. This is hardly comparable to modern analytical balances which typically measure such masses to ± 0.1 mg.

7. **(M)** heat lost by Mg = heat gained by water

$$-\left(1.00 \text{ kg Mg} \times \frac{1000 \text{ g}}{1 \text{ kg}}\right)1.024\frac{J}{g\,^{\circ}C}\left(T_f - 40.0\,^{\circ}C\right) = \left(1.00 \text{ L} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} \times \frac{1.00 \text{ g}}{1 \text{ cm}^3}\right)4.18\frac{J}{g\,^{\circ}C}\left(T_f - 20.0\,^{\circ}C\right)$$

$$-1.024 \times 10^3\, T_f + 4.10 \times 10^4 = 4.18 \times 10^3\, T_f - 8.36 \times 10^4$$

$$4.10 \times 10^4 + 8.36 \times 10^4 = \left(4.18 \times 10^3 + 1.024 \times 10^3\right)T_f \quad \rightarrow \quad 12.46 \times 10^4 = 5.20 \times 10^3\, T_f$$

$$T_f = \frac{12.46 \times 10^4}{5.20 \times 10^3} = 24.0\,^{\circ}C$$

8. **(M)** heat gained by the water = heat lost by the brass

$$150.0 \text{ g} \times 4.18\frac{J}{g\,^{\circ}C} \times \left(T_f - 22.4\,^{\circ}C\right) = -\left(15.2 \text{ cm}^3 \times \frac{8.40 \text{ g}}{1 \text{ cm}^3}\right)0.385\frac{J}{g\,^{\circ}C}\left(T_f - 163\,^{\circ}C\right)$$

$$6.27 \times 10^2\, T_f - 1.40 \times 10^4 = -49.2\, T_f + 8.01 \times 10^3; \quad T_f = \frac{1.40 \times 10^4 + 8.01 \times 10^3}{6.27 \times 10^2 + 49.2} = 32.6\,^{\circ}C$$

9. **(M)** heat lost by copper = heat gained by glycerol

$$-74.8 \text{ g} \times \frac{0.385 \text{ J}}{g\,^{\circ}C} \times \left(31.1\,^{\circ}C - 143.2\,^{\circ}C\right) = 165 \text{ mL} \times \frac{1.26 \text{ g}}{1 \text{ mL}} \times \text{sp.ht.} \times \left(31.1\,^{\circ}C - 24.8\,^{\circ}C\right)$$

$$3.23 \times 10^3 = 1.3 \times 10^3 \times (\text{sp.ht.}) \quad \text{sp.ht.} = \frac{3.23 \times 10^3}{1.3 \times 10^3} = 2.5 \text{ J g}^{-1}\,^{\circ}C^{-1}$$

$$\text{molar heat capacity} = 2.5 \text{ J g}^{-1}\,^{\circ}C^{-1} \times \frac{92.1 \text{ g}}{1 \text{ mol } C_3H_8O_3} = 2.3 \times 10^2 \text{ J mol}^{-1}\,^{\circ}C^{-1}$$

10. **(M)** The additional water simply acts as a heat transfer medium. The essential relationship is heat lost by iron = heat gained by water (of unknown mass).

$$-\left(1.23 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}}\right) 0.449 \frac{J}{g\,^\circ C} (25.6 - 68.5)\,^\circ C = x \text{ g H}_2O \times 4.18 \frac{J}{g\,^\circ C} (25.6 - 18.5)\,^\circ C$$

$$2.37 \times 10^4 \text{ J} = 29.\underline{7}\,x \qquad x = \frac{2.37 \times 10^4}{29.\underline{7}} = 79\underline{8} \text{ g H}_2O \times \frac{1 \text{ mL H}_2O}{1.00 \text{ g H}_2O} = 8.0 \times 10^2 \text{ mL H}_2O$$

11. **(M)** heat capacity = $\dfrac{\text{energy transferred}}{\Delta T} = \dfrac{6.052 \text{ J}}{(25.0 - 20.0 \,^\circ C)} = 1.21$ J/K

*Note: since 1K = 1°C, it is not necessary to convert the temperatures to Kelvin. The change in temperature in both K and °C is the same.

12. **(E)** heat = mass $\times$ sp ht $\times \Delta T$

$$q_{\text{water}} = 6.052\text{J} = 1.24 \text{ g} \times 4.18 \frac{J}{g\,^\circ C} (T_f - 20.0)\,^\circ C$$

$$T_f = 21.2\,^\circ C$$

Heats of Reaction

13. **(E)** heat = $283 \text{ kg} \times \dfrac{1000 \text{ g}}{1 \text{ kg}} \times \dfrac{1 \text{ mol Ca(OH)}_2}{74.09 \text{ g Ca(OH)}_2} \times \dfrac{65.2 \text{ kJ}}{1 \text{ mol Ca(OH)}_2} = 2.49 \times 10^5$ kJ of heat evolved.

14. **(E)** heat energy = $1.00 \text{ gal} \times \dfrac{3.785 \text{ L}}{1 \text{ gal}} \times \dfrac{1000 \text{ mL}}{1 \text{ L}} \times \dfrac{0.703 \text{ g}}{1 \text{ mL}} \times \dfrac{1 \text{ mol C}_8H_{18}}{114.2 \text{ g C}_8H_{18}} \times \dfrac{5.48 \times 10^3 \text{ kJ}}{1 \text{ mol C}_8H_{18}}$

heat energy = 1.28×10^5 kJ

15. **(M)**

(a) heat evolved = $1.325 \text{ g C}_4H_{10} \times \dfrac{1 \text{ mol C}_4H_{10}}{58.123 \text{ g C}_4H_{10}} \times \dfrac{2877 \text{ kJ}}{1 \text{ mol C}_4H_{10}} = 65.59$ kJ

(b) heat evolved = $28.4 \text{ L}_{STP} \text{ C}_4H_{10} \times \dfrac{1 \text{ mol C}_4H_{10}}{22.414 \text{ L}_{STP} \text{ C}_4H_{10}} \times \dfrac{2877 \text{ kJ}}{1 \text{ mol C}_4H_{10}} = 3.65 \times 10^3$ kJ

(c) Use the ideal gas equation to determine the amount of propane in moles and multiply this amount by 2877 kJ heat produced per mole.

$$\text{heat evolved} = \frac{\left(738 \text{ mmHg} \times \dfrac{1\text{atm}}{760 \text{ mmHg}}\right) \times 12.6\text{L}}{\dfrac{0.08206 \text{ L atm}}{\text{mol K}} \times (273.2 + 23.6)\text{ K}} \times \frac{2877 \text{ kJ}}{1 \text{ mol C}_4H_{10}} = 1.45 \times 10^3 \text{ kJ}$$

16. **(M)**

(a) $q = \dfrac{-29.4 \text{ kJ}}{0.584 \text{ g C}_3H_8} \times \dfrac{44.10 \text{ g C}_3H_8}{1 \text{ mol C}_3H_8} = -2.22 \times 10^3$ kJ / mol C_3H_8

(b) $\quad q = \dfrac{-5.27 \text{ kJ}}{0.136 \text{ g } C_{10}H_{16}O} \times \dfrac{152.24 \text{ g } C_{10}H_{16}O}{1 \text{ mol } C_{10}H_{16}O} = -5.90 \times 10^3 \text{ kJ/mol } C_{10}H_{16}O$

(c) $\quad q = \dfrac{-58.3 \text{ kJ}}{2.35 \text{ mL } (CH_3)_2 CO} \times \dfrac{1 \text{ mL}}{0.791 \text{ g}} \times \dfrac{58.08 \text{ g} (CH_3)_2 CO}{1 \text{ mol } (CH_3)_2 CO} = -1.82 \times 10^3 \text{ kJ/mol } (CH_3)_2 CO$

17. **(M)**

(a) $\quad \text{mass} = 2.80 \times 10^7 \text{ kJ} \times \dfrac{1 \text{ mol } CH_4}{890.3 \text{ kJ}} \times \dfrac{16.04 \text{ g } CH_4}{1 \text{ mol } CH_4} \times \dfrac{1 \text{ kg}}{1000 \text{ g}} = 504 \text{ kg } CH_4.$

(b) First determine the moles of CH_4 present, with the ideal gas law.

$$\text{mol } CH_4 = \dfrac{\left(768 \text{ mmHg} \times \dfrac{1 \text{ atm}}{760 \text{ mmHg}}\right) 1.65 \times 10^4 \text{ L}}{0.08206 \dfrac{\text{L atm}}{\text{mol K}} \times (18.6 + 273.2) \text{ K}} = 696 \text{ mol } CH_4$$

$$\text{heat energy} = 696 \text{ mol } CH_4 \times \dfrac{-890.3 \text{ kJ}}{1 \text{ mol } CH_4} = -6.20 \times 10^5 \text{ kJ of heat energy}$$

(c) $\quad V_{H_2O} = \dfrac{6.21 \times 10^5 \text{ kJ} \times \dfrac{1000 \text{ J}}{1 \text{ kJ}}}{4.18 \dfrac{\text{J}}{\text{g }°C} (60.0 - 8.8)°C} \times \dfrac{1 \text{ mL } H_2O}{1 \text{ g}} = 2.90 \times 10^6 \text{ mL} = 2.90 \times 10^3 \text{ L } H_2O$

18. **(M)** The combustion of 1.00 L (STP) of synthesis gas produces 11.13 kJ of heat. The volume of synthesis gas needed to heat 40.0 gal of water is found by first determining the quantity of heat needed to raise the temperature of the water.

$$\text{heat water} = \left(40.0 \text{ gal} \times \dfrac{3.785 \text{ L}}{1 \text{ gal}} \times \dfrac{1000 \text{ mL}}{1 \text{ L}} \times \dfrac{1.00 \text{ g}}{1 \text{ mL}}\right) 4.18 \dfrac{\text{J}}{\text{g }°C} (65.0 - 15.2)°C$$

$$= 3.15 \times 10^7 \text{ J} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}} = 3.15 \times 10^4 \text{ kJ}$$

$$\text{gas volume} = 3.15 \times 10^4 \text{ kJ} \times \dfrac{1 \text{ L (STP)}}{11.13 \text{ kJ of heat}} = 2.83 \times 10^3 \text{ L at STP}$$

19. **(M)** Since the molar mass of H_2 (2.0 g/mol) is $\frac{1}{16}$ of the molar mass of O_2 (32.0 g/mol) and only twice as many moles of H_2 are needed as O_2, we see that $O_2(g)$ is the limiting reagent in this reaction.

$$\dfrac{180.}{2} \text{ g } O_2 \times \dfrac{1 \text{ mol } O_2}{32.0 \text{ g } O_2} \times \dfrac{241.8 \text{ kJ heat}}{0.500 \text{ mol } O_2} = 1.36 \times 10^3 \text{ kJ heat}$$

20. **(M)** The amounts of the two reactants provided are the same as their stoichiometric coefficients in the balanced equation. Thus 852 kJ of heat is given off by the reaction. We can use this quantity of heat, along with the specific heat of the mixture, to determine the temperature change that will occur if all of the heat is retained in the reaction mixture. We make use of the fact that $\text{mass} \times \text{sp.ht.} \times \Delta T$.

$$\text{heat} = 8.52 \times 10^5 \ \text{J} = \left(\left(1 \ \text{mol Al}_2\text{O}_3 \times \frac{102 \ \text{g Al}_2\text{O}_3}{1 \ \text{mol Al}_2\text{O}_3}\right) + \left(2 \ \text{mol Fe} \times \frac{55.8 \ \text{g Fe}}{1 \ \text{mol Fe}}\right)\right) \frac{0.8 \ \text{J}}{\text{g}^\circ\text{C}} \times \Delta T$$

$$\Delta T = \frac{8.52 \times 10^5 \ \text{J}}{214 \ \text{g} \times 0.8 \ \text{J g}^{-1} \, ^\circ\text{C}^{-1}} = 5 \times 10^3 \, ^\circ\text{C}$$

The temperature needs to increase from 25°C to 1530°C or $\Delta T = 1505^\circ\text{C} = 1.5 \times 10^3 \, ^\circ\text{C}$. Since the actual ΔT is more than three times as large as this value, the iron indeed will melt, even if a large fraction of the heat evolved is lost to the surroundings and is not retained in the products.

21. **(M)**

(a) We first compute the heat produced by this reaction, then determine the value of ΔH in kJ/mol KOH.

$$q_{\text{calorimeter}} = (0.205 + 55.9) \ \text{g} \times 4.18 \ \frac{\text{J}}{\text{g}^\circ\text{C}} (24.4 \, ^\circ\text{C} - 23.5 \, ^\circ\text{C}) = 2 \times 10^2 \ \text{J heat} = -q_{\text{rxn}}$$

$$\Delta H = -\frac{2 \times 10^2 \, \text{J} \times \dfrac{1 \ \text{kJ}}{1000 \, \text{J}}}{0.205 \, \text{g} \times \dfrac{1 \, \text{mol KOH}}{56.1 \, \text{g KOH}}} = -5 \times 10^1 \ \text{kJ / mol}$$

(b) The ΔT here is known to just one significant figure (0.9 °C). Doubling the amount of KOH should give a temperature change known to two significant figures (1.6 °C) and using twenty times the mass of KOH should give a temperature change known to three significant figures (16.0 °C). This would require 4.10 g KOH rather than the 0.205 g KOH actually used, and would increase the precision from one part in five to one part in 500, or ~0.2 %. Note that as the mass of KOH is increased and the mass of H_2O stays constant, the assumption of a constant specific heat becomes less valid.

22. **(M)** First we must determine the heat absorbed by the solute during the chemical reaction, q_{rxn}. This is the negative of the heat lost by the solution, q_{soln}. Since the solution (water plus solute) actually gives up heat, the temperature of the solution drops.

$$\text{heat of reaction} = 150.0 \ \text{mL} \times \frac{1 \ \text{L}}{1000 \ \text{mL}} \times \frac{2.50 \ \text{mol KI}}{1 \ \text{L soln}} \times \frac{20.3 \ \text{kJ}}{1 \ \text{mol KI}} = 7.61 \ \text{kJ} = q_{\text{rxn}}$$

$$-q_{\text{rxn}} = q_{soln} = \left(150.0 \ \text{mL} \times \frac{1.30 \ \text{g}}{1 \ \text{mL}}\right) \times \frac{2.7 \ \text{J}}{\text{g}^\circ\text{C}} \times \Delta T \quad \Delta T = \frac{-7.61 \times 10^3 \text{J}}{150.0 \, \text{mL} \times \dfrac{1.30 \, \text{g}}{1 \, \text{mL}} \times \dfrac{2.7 \, \text{J}}{\text{g} \ ^\circ\text{C}}} = -14^\circ\text{C}$$

$\text{final } T = \text{initial } T + \Delta T = 23.5^\circ\text{C} - 14^\circ\text{C} = 10.^\circ\text{C}$

23. **(M)** Let x be the mass, (in grams), of NH_4Cl added to the water.

heat $=$ mass $\times$ sp.ht. $\times \Delta T$

$$x \times \frac{1 \ \text{mol} \ NH_4Cl}{53.49 \ \text{g} \ NH_4Cl} \times \frac{14.7 \ \text{kJ}}{1 \ \text{mol} \ NH_4Cl} \times \frac{1000 \ \text{J}}{1 \ \text{kJ}} = -\left(\left(1400 \ \text{mL} \times \frac{1.00 \ \text{g}}{1 \ \text{mL}}\right) + x\right) 4.18 \frac{\text{J}}{\text{g} \, ^\circ \text{C}} (10. - 25)^\circ \text{C}$$

$$275 \, x = 8.8 \times 10^4 + 63 \, x ; \qquad x = \frac{8.8 \times 10^4}{275 - 63} = 4.2 \times 10^2 \ \text{g} \ NH_4Cl$$

Our final value is approximate because of the assumed density (1.00 g/mL). The solution's density probably is a bit larger than 1.00 g/mL. Many aqueous solutions are somewhat more dense than water.

24. **(M)** heat $= 500 \ \text{mL} \times \frac{1 \ \text{L}}{1000 \ \text{mL}} \times \frac{7.0 \ \text{mol NaOH}}{1 \ \text{L soln}} \times \frac{-44.5 \ \text{kJ}}{1 \ \text{mol NaOH}} = -1.6 \times 10^2 \ \text{kJ}$

$=$ heat of reaction $= -$ heat absorbed by solution $\quad$ OR $\quad q_{rxn} = -q_{soln}$

$$\Delta T = \frac{1.6 \times 10^5 \, \text{J}}{500.\,\text{mL} \times \dfrac{1.08 \, \text{g}}{1 \text{mL}} \times \dfrac{4.00 \, \text{J}}{\text{g} \,^\circ\text{C}}} = 74\,^\circ\text{C} \qquad \text{final } T = 21\,^\circ\text{C} + 74\,^\circ\text{C} = 95\,^\circ\text{C}$$

25. **(E)** We assume that the solution volumes are additive; that is, that 200.0 mL of solution is formed. Then we compute the heat needed to warm the solution and the cup, and finally ΔH for the reaction.

$$\text{heat} = \left(200.0 \ \text{mL} \times \frac{1.02 \ \text{g}}{1 \ \text{mL}}\right) 4.02 \frac{\text{J}}{\text{g} \,^\circ\text{C}} \left(27.8 \,^\circ\text{C} - 21.1 \,^\circ\text{C}\right) + 10 \frac{\text{J}}{^\circ\text{C}} \left(27.8 \,^\circ\text{C} - 21.1 \,^\circ\text{C}\right) = 5.6 \times 10^3 \ \text{J}$$

$$\Delta H_{neutr.} = \frac{-5.6 \times 10^3 \, \text{J}}{0.100 \ \text{mol}} \times \frac{1 \ \text{kJ}}{1000 \ \text{J}} = -56 \ \text{kJ/mol} \ \left(-55.6 \ \text{kJ/mol to three significant figures}\right)$$

26. **(M)** Neutralization reaction: $\quad NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

Since NaOH and HCl react in a one-to-one molar ratio, and since there is twice the volume of NaOH solution as HCl solution, but the [HCl] is not twice the [NaOH], the HCl solution is the limiting reagent.

$$\text{heat released} = 25.00 \ \text{mL} \times \frac{1 \ \text{L}}{1000 \ \text{mL}} \times \frac{1.86 \ \text{mol HCl}}{1 \ \text{L}} \times \frac{1 \ \text{mol H}_2\text{O}}{1 \ \text{mol HCl}} \times \frac{-55.84 \ \text{kJ}}{1 \ \text{mol H}_2\text{O}} = -2.60 \ \text{kJ}$$

$=$ heat of reaction $= -$ heat absorbed by solution or $q_{rxn} = -q_{soln}$

$$\Delta T = \frac{2.60 \times 10^3 \, \text{J}}{75.00 \, \text{mL} \times \dfrac{1.02 \, \text{g}}{1 \text{mL}} \times \dfrac{3.98 \, \text{J}}{\text{g} \,^\circ\text{C}}} = 8.54\,^\circ\text{C} \qquad \Delta T = T_{final} - T_i \qquad T_{final} = \Delta T + T_i$$

$T_{final} = 8.54\,^\circ\text{C} + 24.72 \,^\circ\text{C} = 33.26 \,^\circ\text{C}$

27. **(M)**

$$5.0 \text{ L C}_2\text{H}_2 \times \frac{1 \text{ m}^3}{1000 \text{ L}} \times \frac{1.0967 \text{ kg}}{\text{m}^3} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol}}{26.04 \text{ g}} = 0.2106 \text{ mol C}_2\text{H}_2$$

$$\frac{1299.5 \text{ kJ heat evolved}}{\text{mol C}_2\text{H}_2} \times 0.2106 \text{ mol C}_2\text{H}_2 = 272.9 \text{ kJ} = 2.7 \times 10^2 \text{ kJ heat evolved}$$

28. **(M)**

$$273.8 \text{ kJ} \times \frac{1 \text{ mol propane}}{2219.9 \text{ kJ}} = 0.1233 \text{ mol propane}$$

$$0.1233 \text{ mol C}_3\text{H}_8 \times \frac{44.09 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ m}^3}{1.83 \text{ kg}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} = 2.97 \text{ L C}_3\text{H}_8$$

Enthalpy Changes and States of Matter

29. **(M)** $q_{\text{H}_2\text{O(l)}} = q_{\text{H}_2\text{O(s)}}$ $\quad m(\text{sp. ht.})_{\text{H}_2\text{O(l)}}\Delta T_{\text{H}_2\text{O(l)}} = \text{mol}_{\text{H}_2\text{O(s)}}\Delta H_{\text{fus H}_2\text{O(s)}}$

$$(3.50 \text{ mol H}_2\text{O} \times \frac{18.015 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}})(4.184 \frac{\text{J}}{\text{g °C}})(50.0 \text{ °C}) = (\frac{m}{\frac{18.015 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}} \times 6.01 \times 10^3 \frac{\text{J}}{\text{mol}})$$

$13.2 \times 10^3 \text{ J} = m(333.\underline{6} \text{ J g}^{-1})$ $\quad$ Hence, $m = 39.6$ g

30. **(M)** $-q_{\text{lost by steam}} = q_{\text{gained by water}}$

$$-[(5.00 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}})(-40.6 \times 10^3 \frac{\text{J}}{\text{mol}}) + (5.00 \text{ g})(4.184 \frac{\text{J}}{\text{g °C}})(T_\text{f} - 100.0 \text{ °C})]$$

$$= (100.0 \text{ g})(4.184 \frac{\text{J}}{\text{g °C}})(T_\text{f} - 25.0 \text{ °C})$$

$$112\underline{68.4} \text{ J} - 20.92 \frac{\text{J}}{\text{°C}} (T_\text{f}) + 209\underline{2} \text{ J} = 418.\underline{4} \frac{\text{J}}{\text{°C}} (T_\text{f}) - 10,4\underline{60} \text{ J}$$

$$11,2\underline{68.4} \text{ J} + 10,4\underline{60} \text{ J} + 209\underline{2} \text{ J} = 418.\underline{4} \frac{\text{J}}{\text{°C}} (T_\text{f}) + 20.9\underline{2} \frac{\text{J}}{\text{°C}} (T_\text{f}) \quad \text{or} \quad 23.8 \times 10^3 \text{ J} = 439 \text{ J } (T_\text{f})$$

$T_\text{f} = 54.2 \text{ °C}$

31. **(M)** Assume $\text{H}_2\text{O(l)}$ density $= 1.00 \text{ g mL}^{-1}$ (at 28.5 °C) $\quad -q_{\text{lost by ball}} = q_{\text{gained by water}} + q_{\text{vap water}}$

$$-[(125 \text{ g})(0.50 \frac{\text{J}}{\text{g °C}})(100 \text{ °C} - 525 \text{ °C})] = [(75.0 \text{ g})(4.184 \frac{\text{J}}{\text{g °C}})(100.0 \text{ °C} - 28.5 \text{ °C})] + n_{\text{H}_2\text{O}}\Delta H°_{\text{vap}}$$

$$26\underline{562.5} \text{ J} = 224\underline{36.7} \text{ J} + n_{\text{H}_2\text{O}}\Delta H°_{\text{vap}} \text{ (Note: } n_{\text{H}_2\text{O}} = \frac{\text{mass}_{\text{H}_2\text{O}}}{\text{molar mass}_{\text{H}_2\text{O}}})$$

$$4\underline{125.8} \text{ J} = (m_{\text{H}_2\text{O}})(\frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}})(40.6 \times 10^3 \frac{\text{J}}{\text{mol}})$$

$m_{\text{H}_2\text{O}} = 1.\underline{83} \text{ g H}_2\text{O} \cong 2 \text{ g H}_2\text{O}$ (1 sig. fig.)

32. **(E)** $-q_{\text{lost by ball}} = q_{\text{melt ice}}$

$$-[(125\text{ g})(0.50\ \frac{\text{J}}{\text{g }^\circ\text{C}})(0\ ^\circ\text{C} -525\ ^\circ\text{C})] = n_{\text{H}_2\text{O}}\Delta H^\circ_{\text{fus}} = (m_{\text{H}_2\text{O}})(\frac{1\text{ mol H}_2\text{O}}{18.015\text{ g H}_2\text{O}})(6.01 \times 10^3\ \frac{\text{J}}{\text{mol}})$$

$32\underline{812.5}\text{ J} = m_{\text{H}_2\text{O}}(333\underline{.6}\text{ J g}^{-1})$;　　　$m_{\text{H}_2\text{O}} = 98.\underline{4}\text{ g H}_2\text{O} \cong 98\text{ g H}_2\text{O}$.

33. **(E)**

$$\frac{571\text{ kJ}}{\text{kg}} \times \frac{1000\text{ J}}{1\text{ kJ}} = 5.71 \times 10^5\text{ J/kg}$$

$$125.0\text{ J} \times \frac{1\text{ kg}}{5.71 \times 10^5\text{ J}} \times \frac{1000\text{ g}}{1\text{ kg}} \times \frac{1\text{ L}}{1.98\text{ g}} = 0.111\text{ L}$$

34. **(M)** Assume all $N_2(l)$ is converted to $N_2(g)$ when vaporized. The number of moles of $N_2(g)$ can be found by using the ideal gas equation.

$PV = nRT$

$(1.0\text{ atm})(1.0\text{ L}) = n(0.08206\text{ L}\cdot\text{atm/K}\cdot\text{mol})(77.36\text{ K})$

$n = 0.1575\text{ mol} = 0.16\text{ mol (2 sig figs)}$

If 5.56 kJ of energy is needed to vaporize 1 mol of $N_2(l)$, then

$$0.1575\text{ mol} \times \frac{5.56\text{ kJ}}{1\text{ mol}} = 0.876\text{ kJ} = 8.8 \times 10^2\text{ J are needed to vaporize 0.1575 mol.}$$

Calorimetry

35. **(E)** Heat capacity $= \dfrac{\text{heat absorbed}}{\Delta T} = \dfrac{5228\text{ cal}}{4.39\,^\circ\text{C}} \times \dfrac{4.184\text{ J}}{1\text{ cal}} \times \dfrac{1\text{ kJ}}{1000\text{ J}} = 4.98\text{ kJ}/^\circ\text{ C}$

36. **(M)** heat absorbed by calorimeter $= q_{\text{comb}} \times \text{moles} = \text{heat capacity} \times \Delta T$ or $\Delta T = \dfrac{q_{\text{comb}} \times \text{moles}}{\text{heat capacity}}$

(a) $\Delta T = \dfrac{\left(1014.2\dfrac{\text{kcal}}{\text{mol}} \times 4.184\dfrac{\text{kJ}}{\text{kcal}}\right)\left(0.3268\text{ g} \times \dfrac{1\text{ mol C}_8\text{H}_{10}\text{O}_2\text{N}_4}{194.19\text{ g C}_8\text{H}_{10}\text{O}_2\text{N}_4}\right)}{5.136\text{ kJ}/^\circ\text{C}} = 1.390\ ^\circ\text{C}$

$T_f = T_i + \Delta T = 22.43\,^\circ\text{C} + 1.390\,^\circ\text{C} = 23.82\,^\circ\text{C}$

(b) $\Delta T = \dfrac{2444\dfrac{\text{kJ}}{\text{mol}}\left(1.35\text{ mL} \times \dfrac{0.805\text{ g}}{1\text{ mL}} \times \dfrac{1\text{ mol C}_4\text{H}_8\text{O}}{72.11\text{ g C}_4\text{H}_8\text{O}}\right)}{5.136\text{ kJ}/^\circ\text{C}} = 7.17\,^\circ\text{C}$
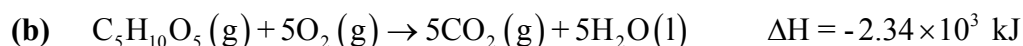
$T_f = 22.43\,^\circ\text{C} + 7.17\,^\circ\text{C} = 29.60\,^\circ\text{C}$

37. **(M)**

(a) $\dfrac{\text{heat}}{\text{mass}} = \dfrac{\text{heat cap.} \times \Delta t}{\text{mass}} = \dfrac{4.728 \text{ kJ}/^\circ\text{C} \times (27.19 - 23.29)^\circ\text{C}}{1.183 \text{ g}} = 15.6 \text{ kJ}/\text{g xylose}$

$\Delta H = \text{heat given off}/\text{g} \times M(\text{g}/\text{mol}) = \dfrac{-15.6 \text{ kJ}}{1 \text{ g C}_5\text{H}_{10}\text{O}_5} \times \dfrac{150.13 \text{ g C}_5\text{H}_{10}\text{O}_5}{1 \text{ mol}}$

$\Delta H = -2.34 \times 10^3 \text{ kJ/mol C}_5\text{H}_{10}\text{O}_5$

(b) $C_5\text{H}_{10}\text{O}_5(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 5\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l})$ $\qquad \Delta H = -2.34 \times 10^3 \text{ kJ}$

38. **(M)** This is first a limiting reactant problem. There is $0.1000 \text{ L} \times 0.300 \text{ M} = 0.0300$ mol HCl and $1.82/65.39 = 0.0278$ mol Zn. Stoichiometry demands 2 mol HCl for every 1 mol Zn. Thus HCl is the limiting reactant. The reaction is exothermic. We neglect the slight excess of Zn(s), and assume that the volume of solution remains 100.0 mL and its specific heat, $4.18 \text{ J g}^{-1}{}^\circ\text{C}^{-1}$. The enthalpy change, in kJ/mol Zn, is

$\Delta H = -\dfrac{100.0 \text{ mL} \times \dfrac{1.00 \text{ g}}{1 \text{ mL}} \times \dfrac{4.18 \text{ J}}{\text{g}^\circ\text{C}} \times (30.5 - 20.3)^\circ\text{C}}{0.0300 \text{ mol HCl} \times \dfrac{1 \text{ mol Zn}}{2 \text{ mol HCl}}} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}} = -284 \text{ kJ/mol Zn reacted}$

39. **(M)**

(a) Because the temperature of the mixture decreases, the reaction molecules (the system) must have absorbed heat from the reaction mixture (the surroundings). Consequently, the reaction must be endothermic.

(b) We assume that the specific heat of the solution is $4.18 \text{ J g}^{-1}{}^\circ\text{C}^{-1}$. The enthalpy change in kJ/mol KCl is obtained by the heat absorbed per gram KCl.

$\Delta H = -\dfrac{(0.75 + 35.0) \text{ g} \dfrac{4.18 \text{ J}}{\text{g}^\circ\text{C}} (23.6 - 24.8)^\circ\text{C}}{0.75 \text{ g KCl}} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}} \times \dfrac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} = +18 \text{ kJ}/\text{mol}$

40. **(M)** As indicated by the negative sign for the enthalpy change, this is an exothermic reaction. Thus the energy of the system should increase.

$q_{\text{rxn}} = 0.136 \text{ mol KC}_2\text{H}_3\text{O}_2 \times \dfrac{-15.3 \text{ kJ}}{1 \text{ mol KC}_2\text{H}_3\text{O}_2} \times \dfrac{1000 \text{ J}}{1 \text{ kJ}} = -2.08 \times 10^3 \text{ J} = -q_{\text{calorim}}$

Now, we assume that the density of water is 1.00 g/mL, the specific heat of the solution in the calorimeter is $4.18 \text{ J g}^{-1}{}^\circ\text{C}^{-1}$, and no heat is lost by the calorimeter.

$q_{\text{calorim}} = 2.08 \times 10^3 \text{ J} = \left(\left(525 \text{ mL} \times \dfrac{1.00 \text{ g}}{1 \text{ mL}}\right) + \left(0.136 \text{ mol KC}_2\text{H}_3\text{O}_2 \times \dfrac{98.14 \text{ g}}{1 \text{ mol KC}_2\text{H}_3\text{O}_2}\right)\right)$

$\times \dfrac{4.18 \text{ J}}{\text{g}^\circ\text{C}} \times \Delta T = 2.25 \times 10^3 \Delta T$

$\Delta T = \dfrac{2.08 \times 10^3}{2.25 \times 10^3} = +0.924\,^\circ\text{C}$ $\qquad T_{\text{final}} = T_{\text{initial}} + \Delta T = 25.1\,^\circ\text{C} + 0.924\,^\circ\text{C} = 26.0\,^\circ\text{C}$

41. **(M)** To determine the heat capacity of the calorimeter, recognize that the heat evolved by the reaction is the negative of the heat of combustion.

$$\text{heat capacity} = \frac{\text{heat evolved}}{\Delta T} = \frac{1.620\,g\,C_{10}H_8 \times \dfrac{1\,mol\,C_{10}H_8}{128.2\,g\,C_{10}H_8} \times \dfrac{5156.1\,kJ}{1\,mol\,C_{10}H_8}}{8.44\,°C} = 7.72\,kJ/°C$$

42. **(M)** Note that the heat evolved is the negative of the heat absorbed.

$$\text{heat capacity} = \frac{\text{heat evolved}}{\Delta T} = \frac{1.201\,g \times \dfrac{1\,mol\,C_7H_6O_3}{138.12\,g\,C_7H_6O_3} \times \dfrac{3023\,kJ}{1\,mol\,C_7H_6O_3}}{(29.82 - 23.68)\,°C} = 4.28\,kJ/°C$$

43. **(M)** The temperature should increase as the result of an exothermic combustion reaction.

$$\Delta T = 1.227\ g\ C_{12}H_{22}O_{11} \times \frac{1\ mol\ C_{12}H_{22}O_{11}}{342.3\ g\ C_{12}H_{22}O_{11}} \times \frac{5.65 \times 10^3\ kJ}{1\ mol\ C_{12}H_{22}O_{11}} \times \frac{1\,°C}{3.87\ kJ} = 5.23\,°C$$

44. **(M)** $q_{comb} = \dfrac{-11.23\,°C \times 4.68\,kJ/°C}{1.397\,g\,C_{10}H_{14}O \times \dfrac{1\,mol\,C_{10}H_{14}O}{150.2\,g\,C_{10}H_{14}O}} = -5.65 \times 10^3\ kJ\,/\,mol\,C_{10}H_{14}O$

45. **(M)**

$$5.0\ g\ NaCl \times \frac{1\ mol}{58.44\ g} = 0.08556\ mol\ NaCl$$

$$0.08556\ mol\ NaCl \times \frac{3.76\ kJ}{1\ mol} = 0.322\ kJ = 322\ J$$

$$q = mass_{H_2O} \times \text{specific heat} \times \Delta T$$

$$322\ J = mass_{H_2O} \times 4.18\ J/g\,°C \times 5.0\,°C$$

$$mass_{H_2O} = 15\ g$$

46. **(M)** heat lost by gold = heat gained by water

$$-10.5\ g \times \text{specific heat of gold} \times (31.0\text{-}78.3\,°C) = 50\ g \times \frac{4.18\ J}{g\,°C} \times (31.0 - 23.7\,°C)$$

$$496.65 \times \text{specific heat of gold} = 1525.7$$

$$\text{specific heat of gold} = 3.07\ \frac{J}{g\,°C} = 3.07\ \frac{J}{g\,K}$$

Since the specific heat of the sample does not equal the specific heat of pure gold that is given in the problem, the sample is not pure gold.

Pressure-Volume Work

47. **(M)**

(a) $-P\Delta V = 3.5 \text{ L} \times (748 \text{ mmHg})\left(\dfrac{1\,\text{atm}}{760\,\text{mmHg}}\right) = $ -3.4$\underline{4}$ L atm or -3.4 L atm

(b) 1 L kPa = 1 J, hence,

-3.4$\underline{4}$ L atm $\times \left(\dfrac{101.325 \text{ kPa}}{1 \text{ atm}}\right) \times \left(\dfrac{1\,\text{J}}{1\,\text{L}\,\text{kPa}}\right) = $ -3.4$\underline{9}$ × 10² J or -3.5 × 10² J

(c) -3.4$\underline{9}$ × 10² J $\times \left(\dfrac{1 \text{ cal}}{4.184 \text{ J}}\right) = $ -83.$\underline{4}$ cal or -83 cal

48. **(E)** $w = -P\Delta V = -1.23 \text{ atm} \times (3.37 \text{ L} - 5.62 \text{ L}) \times \left(\dfrac{101.325 \text{ kPa}}{1 \text{ atm}}\right) \times \left(\dfrac{1\,\text{J}}{1\,\text{L}\,\text{kPa}}\right) = 280.$ J

That is, 280. J of work is done on the gas by the surroundings.

49. **(E)** When the Ne(g) sample expands into an evacuated vessel it does not push aside any matter, hence no work is done.

50. **(E)** Yes, the gas from the aerosol does work. The gas pushes aside the atmosphere.

51. **(M)**
(a) No pressure-volume work is done (no gases are formed or consumed).
(b) $2 \text{ NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ $\Delta n_{gas} = -1$ mole. Work is done on the system by the surroundings (compression).
(c) $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$. Formation of a gas, $\Delta n_{gas} = +1$ mole, results in an expansion. The system does work on the surroundings.

52. **(M)**
(a) $2 \text{ NO}(g) + \text{O}_2(g) \rightarrow 2 \text{ NO}_2(g)$ $\Delta n_{gas} = -1$ mole. Work is done on the system by the surroundings (compression).
(b) $\text{MgCl}_2(aq) + 2 \text{ NaOH}(aq) \rightarrow \text{Mg(OH)}_2(s) + 2 \text{ NaCl}(aq)$ $\Delta n_{gas} = 0$, no pressure-volume work is done.
(c) $\text{CuSO}_4(s) + 5 \text{ H}_2\text{O}(g) \rightarrow \text{CuSO}_4 \bullet 5 \text{ H}_2\text{O}(s)$ $\Delta n_{gas} = -5$ moles. Work is done on the system by the surroundings (compression).

53. **(E)** We can either convert pressure from atm to Pascals, or convert work from Joules to L·atm. We opt for the latter. Since the conversion between J and L·atm is 101.33 J/(L·atm), the amount of work is 325 J × (1 L·atm/101.33 J) = 3.207 L·atm. Therefore,
W = -PΔV
3.207 L·atm = (1.0 atm) ΔV. Solving for ΔV, we get a volume of 3.21 L.

54. **(E)** We note that the work done on the object imparts a potential energy in that object after the work is done. Therefore,

work = -e_p

$e_p = m \times g \times h = (1.23 \text{ kg})(9.8 \text{ m/s}^2)(4.5 \text{ m}) = 54.24 \text{J}$
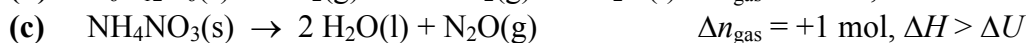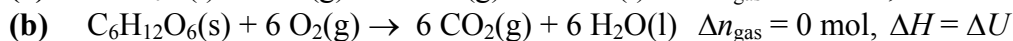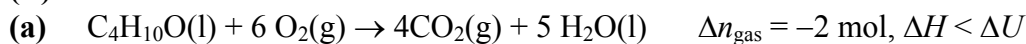
work = -54 J

First Law of Thermodynamics

55. **(E)**
    (a) $\Delta U = q + w = +58 \text{ J} + (-58 \text{ J}) = 0$
    (b) $\Delta U = q + w = +125 \text{ J} + (-687 \text{ J}) = -562 \text{ J}$
    (c) $280 \text{ cal} \times (4.184 \frac{\text{J}}{\text{cal}}) = 117\underline{1.52} \text{ J} = 1.17 \text{ kJ}$ $\Delta U = q + w = -1.17 \text{ kJ} + 1.25 \text{ kJ} = 0.08 \text{ kJ}$

56. **(E)**
    (a) $\Delta U = q + w = +235 \text{ J} + 128 \text{ J} = 363 \text{ J}$
    (b) $\Delta U = q + w = -145 \text{ J} + 98 \text{ J} = -47 \text{ J}$
    (c) $\Delta U = q + w = 0 \text{ kJ} + -1.07 \text{ kJ} = -1.07 \text{ kJ}$

57. **(E)**
    (a)   Yes, the gas does work (w = negative value).
    (b)   Yes, the gas exchanges energy with the surroundings, it absorbs energy.
    (c)   The temperature of the gas stays the same if the process is isothermal.
    (d)   ΔU for the gas must equal zero by definition (temperature is not changing).

58. **(E)**
    (a)   Yes, the gas does work (w = negative value).
    (b)   The internal energy of the gas decreases (energy is expended to do work).
    (c)   The temperature of the gas should decrease, as it cannot attain thermal equilibrium with its surroundings.

59. **(E)** This situation is impossible. An ideal gas expanding isothermally means that $\Delta U = 0 = q + w$, or $w = -q$, not $w = -2q$.

60. **(E)** If a gas is compressed adiabatically, the gas will get hotter. Raise the temperature of the surroundings to an even higher temperature and heat will be transferred to the gas.

61. **(E)** We note that since the charge of the system is going from 10 to 5, the net flow of the charge is negative. Therefore, w = (5 C – 10 C) = -5 C. Voltage (V) is J/C. The internal energy of the system is:
ΔU = q + w = -45 J + (100 J/C)(-5 C) = -45 J + (-500 J) = -545 J

62. **(E)** Obviously, w = $f \Delta L$. Plugging in the appropriate values gives the following:
ΔU = $(10 \times 10^{-12} \text{ N})(10 \times 10^{-12} \text{ m}) = 1 \times 10^{-22} \text{ J}$

Relating ΔH and ΔU

63. **(E)** According to the First Law of Thermodynamics, the answer is (c). Both (a) q_v and (b) q_p are heats of chemical reaction carried out under conditions of constant volume and constant pressure, respectively. Both ΔU and ΔH incorporate terms related to work as well as heat.

64. **(E)**
  (a) $C_4H_{10}O(l) + 6\ O_2(g) \rightarrow 4CO_2(g) + 5\ H_2O(l)$ $\Delta n_{gas} = -2$ mol, $\Delta H < \Delta U$
  (b) $C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$ $\Delta n_{gas} = 0$ mol, $\Delta H = \Delta U$
  (c) $NH_4NO_3(s) \rightarrow 2\ H_2O(l) + N_2O(g)$ $\Delta n_{gas} = +1$ mol, $\Delta H > \Delta U$

65. **(M)** $C_3H_8O(l) + 9/2\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$ $\Delta n_{gas} = -1.5$ mol
  (a) $\Delta U = -33.41 \dfrac{kJ}{g} \times \dfrac{60.096\ g\ C_3H_8O}{1\ mol\ C_3H_8O} = -2008 \dfrac{kJ}{mol}$
  (b) $\Delta H = \Delta U - w, = \Delta U - (-P\Delta V) = \Delta U - (-\Delta n_{gas}RT) = \Delta U + \Delta n_{gas}RT$
  $\Delta H = -2008 \dfrac{kJ}{mol} + (-1.5\ mol)(\dfrac{8.3145 \times 10^{-3}\ kJ}{K\ mol})(298.15\ K) = -2012 \dfrac{kJ}{mol}$

66. **(M)** $C_{10}H_{14}O(l) + 13\ O_2(g) \rightarrow 10\ CO_2(g) + 7\ H_2O(l)$ $\Delta n_{gas} = -3$ mol
  $q_{bomb} = q_v = \Delta U = -5.65 \times 10^3\ kJ = \Delta U$

  $\Delta H = \Delta U - w$; where $w = (-\Delta n_{gas}RT) = -(-3\ mol)(\dfrac{8.3145 \times 10^{-3}\ kJ}{K\ mol})(298.15\ K) = +7.4\ kJ$

  $\Delta H = -5.65 \times 10^3\ kJ - 7.4\ kJ = -5.66 \times 10^3\ kJ$
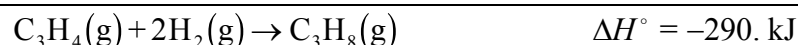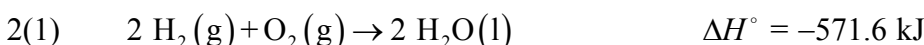
Hess's Law

67. **(E)** The formation reaction for $NH_3(g)$ is $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$. The given reaction is two-thirds the reverse of the formation reaction. The sign of the enthalpy is changed and it is multiplied by two-thirds. Thus, the enthalpy of the given reaction is $-(-46.11\ kJ) \times \frac{2}{3} = +30.74\ kJ$.

68. **(M)**
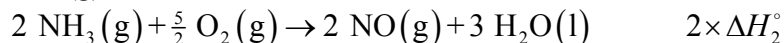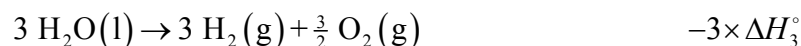 $-(1)$ $CO(g) \rightarrow C(graphite) + \frac{1}{2}O_2(g)$ $\Delta H° = +110.54\ kJ$
  $+(2)$ $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -393.51\ kJ$
  _____
      $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -282.97\ kJ$

69. **(M)**
  $-(3)$ $3\ CO_2(g) + 4\ H_2O(l) \rightarrow C_3H_8(g) + 5\ O_2(g)$ $\Delta H° = +2219.1\ kJ$
  $+(2)$ $C_3H_4(g) + 4\ O_2(g) \rightarrow 3\ CO_2(g) + 2\ H_2O(l)$ $\Delta H° = -1937\ kJ$
  $2(1)$ $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ $\Delta H° = -571.6\ kJ$
  _____
      $C_3H_4(g) + 2H_2(g) \rightarrow C_3H_8(g)$ $\Delta H° = -290.\ kJ$
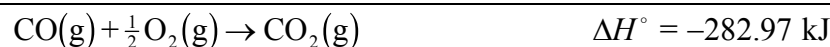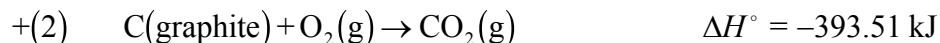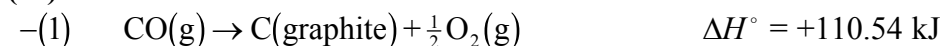
70. **(M)** The second reaction is the only one in which NO(g) appears; it must be run twice to produce 2NO(g).

$$2\ NH_3(g) + \tfrac{5}{2}\ O_2(g) \rightarrow 2\ NO(g) + 3\ H_2O(l) \qquad 2 \times \Delta H_2^\circ$$

The first reaction is the only one that eliminates $NH_3(g)$; it must be run twice to eliminate $2NH_3$.

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g) \qquad 2 \times \Delta H_1^\circ$$
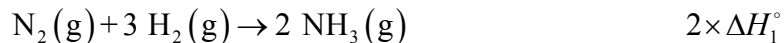
We triple and reverse the third reaction to eliminate $3H_2(g)$.

$$3\ H_2O(l) \rightarrow 3\ H_2(g) + \tfrac{3}{2}\ O_2(g) \qquad -3 \times \Delta H_3^\circ$$

$$\text{Result}: N_2(g) + O_2(g) \rightarrow 2\ NO(g) \qquad \Delta H_{rxn} = 2 \times \Delta H_1 + 2 \times \Delta H_2 - 3 \times \Delta H_3$$

71. **(M)**

$$2HCl(g) + C_2H_4(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_4Cl_2(l) + H_2O(l) \quad \Delta H^\circ = -318.7 \text{ kJ}$$
$$Cl_2(g) + H_2O(l) \rightarrow 2HCl(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H^\circ = 0.5(+202.4) = +101.2 \text{ kJ}$$
$$\overline{C_2H_4(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(l) \qquad\qquad\quad \Delta H^\circ = -217.5 \text{ kJ}}$$

72. **(M)**

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l) \qquad\qquad \Delta H^\circ = -622.2 \text{ kJ}$$
$$2H_2O_2(l) \rightarrow 2H_2(g) + 2O_2(g) \qquad\qquad \Delta H^\circ = -2(-187.8 \text{ kJ}) = +375.6 \text{ kJ}$$
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad\qquad \Delta H^\circ = 2(-285.8 \text{ kJ}) = -571.6 \text{ kJ}$$
$$\overline{N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l) \qquad \Delta H^\circ = -818.2 \text{ kJ}}$$

73. **(M)**

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad\qquad \Delta H^\circ = -283.0 \text{ kJ}$$
$$3C(\text{graphite}) + 6H_2(g) \rightarrow 3CH_4(g) \qquad \Delta H^\circ = 3(-74.81) = -224.43 \text{ kJ}$$
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad\qquad \Delta H^\circ = 2(-285.8) = -571.6 \text{ kJ}$$
$$3CO(g) \rightarrow \tfrac{3}{2}O_2(g) + 3C(\text{graphite}) \qquad \Delta H^\circ = 3(+110.5) = +331.5 \text{ kJ}$$
$$\overline{4CO(g) + 8H_2(g) \rightarrow CO_2(g) + 3CH_4(g) + 2H_2O(l) \quad \Delta H^\circ = -747.5 \text{ kJ}}$$

74. **(M)**

$$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g) \qquad\quad \Delta H^\circ = -1077 \text{ kJ}$$
$$2S(s) + Cl_2(g) \rightarrow S_2Cl_2(l) \qquad\qquad\qquad \Delta H^\circ = -58.2 \text{ kJ}$$
$$C(s) + 2Cl_2(g) \rightarrow CCl_4(l) \qquad\qquad\qquad \Delta H^\circ = -135.4 \text{ kJ}$$
$$2SO_2(g) \rightarrow 2S(s) + 2O_2(g) \qquad\qquad\quad \Delta H^\circ = -2(-296.8 \text{ kJ}) = +593.6 \text{ kJ}$$
$$CO_2(g) \rightarrow C(s) + O_2(g) \qquad\qquad\qquad \Delta H^\circ = -(-393.5 \text{ kJ}) = +393.5 \text{ kJ}$$
$$\overline{CS_2(l) + 3Cl_2(g) \rightarrow CCl_4(l) + S_2Cl_2(l) \qquad \Delta H^\circ = -284 \text{ kJ}}$$

75. (M)

$$CH_4(g) + CO_2(g) \rightarrow 2CO(g) + 2H_2(g) \qquad \Delta H° = +247 \text{ kJ}$$

$$2CH_4(g) + 2H_2O(g) \rightarrow 2CO(g) + 6H_2(g) \qquad \Delta H° = 2(+206 \text{ kJ}) = +412 \text{ kJ}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H° = -802 \text{ kJ}$$

$$\overline{4CH_4(g) + 2O_2(g) \rightarrow 4CO(g) + 8H_2(g)} \qquad \Delta H° = -143 \text{ kJ}$$

$\div 4$ produces $CH_4(g) + \frac{1}{2}O_2(g) \rightarrow CO(g) + 2H_2(g)$ $\quad \Delta H° = -35.8 \text{ kJ}$

76. (M)

The thermochemical combustion reactions follow.

$$C_4H_6(g) + \tfrac{11}{2} O_2(g) \rightarrow 4 CO_2(g) + 3 H_2O(l) \qquad \Delta H° = -2540.2 \text{ kJ}$$
$$C_4H_{10}(g) + \tfrac{13}{2} O_2(g) \rightarrow 4 CO_2(g) + 5 H_2O(l) \qquad \Delta H° = -2877.6 \text{ kJ}$$
$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta H° = -285.85 \text{ kJ}$$
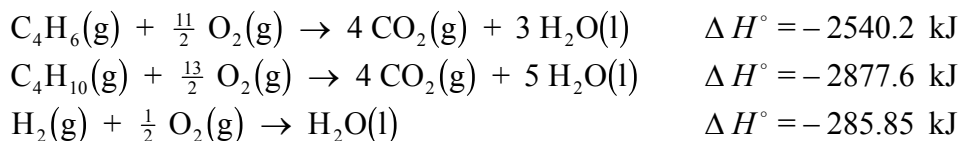
Then these equations are combined in the following manner.

$$C_4H_6(g) + \tfrac{11}{2}O_2(g) \rightarrow 4CO_2(g) + 3H_2O(l) \qquad \Delta H° = -2540.2 \text{ kJ}$$

$$4CO_2(g) + 5H_2O(l) \rightarrow C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \qquad \Delta H° = -(-2877.6 \text{ kJ}) = +2877.6 \text{ kJ}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H° = 2(-285.8 \text{ kJ}) = -571.6 \text{ kJ}$$

$$\overline{C_4H_6(g) + 2H_2(g) \rightarrow C_4H_{10}(g)} \qquad \Delta H° = -234.2 \text{ kJ}$$

77. (M)

$$C_6H_{12}O_6(s) + 6 O_2(g) \rightarrow 6 CO_2(g) + 6 H_2O(l) \qquad \Delta H° = -2808 \text{ kJ}$$
$$6 CO_2(g) + 6 H_2O(l) \rightarrow 2 CH_3CH(OH)COOH(s) + 6 O_2(g) \qquad \Delta H° = 2(1344) \text{ kJ}$$

$$\overline{C_6H_{12}O_6(s) \rightarrow 2 CH_3CH(OH)COOH(s)} \qquad \Delta H° = -120. \text{ kJ}$$

78. (M)

$$\tfrac{1}{2} [C_6H_{12}O_6(s) + 6 O_2(g) \rightarrow 6 CO_2(g) + 6 H_2O(l)] \qquad \Delta H° = \tfrac{1}{2} (-2808) \text{ kJ}$$
$$\tfrac{1}{2} [2 CH_3CH_2OH(l) + 2 CO_2(g) \rightarrow C_6H_{12}O_6(s)] \qquad \Delta H° = \tfrac{1}{2} (72) \text{ kJ}$$

$$\overline{CH_3CH_2OH(l) + 3 O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(l)} \qquad \Delta H° = -1368 \text{ kJ}$$

Standard Enthalpies of Formation

79. (M)

(a) $\Delta H° = \Delta H_f°[C_2H_6(g)] + \Delta H_f°[CH_4(g)] - \Delta H_f°[C_3H_8(g)] - \Delta H_f°[H_2(g)]$

$\Delta H° = (-84.68 - 74.81 - (-103.8) - 0.00) \text{ kJ} = -55.7 \text{ kJ}$

(b) $\Delta H^\circ = 2\Delta H_f^\circ[SO_2(g)] + 2\Delta H_f^\circ[H_2O(l)] - 2\Delta H_f^\circ[H_2S(g)] - 3\Delta H_f^\circ[O_2(g)]$

$\Delta H^\circ = (2(-296.8) + 2(-285.8) - 2(-20.63) - 3(0.00))\,kJ = -1124\ kJ$

80. **(E)** $\Delta H^\circ = \Delta H_f^\circ[H_2O(l)] + \Delta H_f^\circ[NH_3(g)] - \Delta H_f^\circ[NH_4^+(aq)] - \Delta H_f^\circ[OH^-(aq)]$

$\Delta H^\circ = (-285.8 + (-46.11) - (-132.5) - (-230.0))\,kJ = +30.6\ kJ$

81. **(M)**

$ZnO(s) + SO_2(g) \rightarrow ZnS(s) + \tfrac{3}{2}O_2(g); \qquad \Delta H^\circ = -(-878.2\ kJ)/2 = +439.1\ kJ$

$439.1\ kJ = \Delta H_f^\circ[ZnS(s)] + \tfrac{3}{2}\Delta H_f^\circ[O_2(g)] - \Delta H_f^\circ[ZnO(s)] - \Delta H_f^\circ[SO_2(g)]$

$439.1\ kJ = \Delta H_f^\circ[ZnS(s)] + \tfrac{3}{2}(0.00\ kJ) - (-348.3\ kJ) - (-296.8\ kJ)$

$\Delta H_f^\circ[ZnS(s)] = (439.1 - 348.3 - 296.8)\,kJ = -206.0\ kJ/mol$

82. **(M)** Most clearly established in Figure 7-18 is the point that the enthalpies of formation for alkane hydrocarbons are negative and that they become more negative as the length of the hydrocarbon chain increases (~20 kJ per added CH_2 unit). For three hydrocarbons of comparable chain length, C_2H_6, C_2H_4, and C_2H_6, we can also infer that the one having only single bonds (C_2H_6) has the most negative enthalpy of formation. The presence of a carbon-to-carbon double bond (C_2H_4) makes the enthalpy of formation more positive, while the presence of a triple bond (C_2H_2), makes it more positive still.

83. **(E)** $\Delta H^\circ = 4\Delta H_f^\circ[HCl(g)] + \Delta H_f^\circ[O_2(g)] - 2\Delta H_f^\circ[Cl_2(g)] - 2\Delta H_f^\circ[H_2O(l)]$

$= 4(-92.31) + (0.00) - 2(0.00) - 2(-285.8) = +202.4\ kJ$

84. **(E)** $\Delta H^\circ = 2\Delta H_f^\circ[Fe(s)] + 3\Delta H_f^\circ[CO_2(g)] - \Delta H_f^\circ[Fe_2O_3(s)] - 3\Delta H_f^\circ[CO(g)]$

$= 2(0.00) + 3(-393.5) - (-824.2) - 3(-110.5) = -24.8\ kJ$

85. **(E)** Balanced equation: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta H^\circ = 2\Delta H_f^\circ[CO_2(g)] + 3\Delta H_f^\circ[H_2O(l)] - \Delta H_f^\circ[C_2H_5OH(l)] - 3\Delta H_f^\circ[O_2(g)]$

$= 2(-393.5) + 3(-285.8) - (-277.7) - 3(0.00) = -1366.7\ kJ$

86. **(M)** First we must determine the value of ΔH_f° for $C_5H_{12}(l)$.

Balanced combustion equation: $C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$

$\Delta H^\circ = -3509\ kJ = 5\Delta H_f^\circ[CO_2(g)] + 6\Delta H_f^\circ[H_2O(l)] - \Delta H_f^\circ[C_5H_{12}(l)] - 8\Delta H_f^\circ[O_2(g)]$

$= 5(-393.5) + 6(-285.8) - \Delta H_f^\circ[C_5H_{12}(l)] - 8(0.00) = -3682\ kJ - \Delta H_f^\circ[C_5H_{12}(l)]$

$\Delta H_f^\circ[C_5H_{12}(l)] = -3682 + 3509 = -173\ kJ/mol$

Then use this value to determine the value of ΔH° for the reaction in question.

$\Delta H^\circ = \Delta H_f^\circ[C_5H_{12}(l)] + 5\Delta H_f^\circ[H_2O(l)] - 5\Delta H_f^\circ[CO(g)] - 11\Delta H_f^\circ[H_2(g)]$

$= -173 + 5(-285.8) - 5(-110.5) - 11(0.00) = -1050\ kJ$

87. **(E)** $\Delta H° = -397.3 \text{ kJ} = \Delta H_f°[CCl_4(g)] + 4\Delta H_f°[HCl(g)] - \Delta H_f°[CH_4(g)] - 4\Delta H_f°[Cl_2(g)]$

$= \Delta H_f°[CCl_4(g)] + (4(-92.31) - (-74.81) - 4(0.00))\text{kJ} = \Delta H_f°[CCl_4(g)] - 294.4 \text{ kJ}$

$\Delta H_f°[CCl_4(g)] = (-397.3 + 294.4) \text{ kJ} = -102.9 \text{ kJ/mol}$

88. **(E)** $\Delta H° = -8326 \text{ kJ} = 12\Delta H_f°[CO_2(g)] + 14\Delta H_f°[H_2O(g)] - 2\Delta H_f°[C_6H_{14}(l)] - 19\Delta H_f°[O_2(g)]$

$\Delta H° = (12(-393.5) + 14(-285.8))\text{kJ} - 2\Delta H_f°[C_6H_{14}(l)] - 19(0 \text{ kJ}) = -8723 \text{ kJ} - 2\Delta H_f°[C_6H_{14}(l)]$

$\Delta H_f°[C_6H_{14}(l)] = \dfrac{+8326 - 8723}{2} = -199 \text{ kJ / mol}$

89. **(E)** $\Delta H° = \Delta H_f°[Al(OH)_3(s)] - \Delta H_f°[Al^{3+}(aq)] - 3\Delta H_f°[OH^-(aq)]$

$= ((-1276) - (-531) - 3(-230.0))\text{kJ} = -55 \text{ kJ}$

90. **(M)** $\Delta H° = \Delta H_f°[Mg^{2+}(aq)] + 2\Delta H_f°[NH_3(g)] + 2\Delta H_f°[H_2O(l)] - \Delta H_f°[Mg(OH)_2(s)] - 2\Delta H_f°[NH_4^+(aq)]$

$= ((-466.9) + 2(-46.11) + 2(-285.8) - (-924.5) - 2(-132.5))\text{kJ} = +58.8 \text{ kJ}$

91. **(M)** Balanced equation: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$\Delta H° = \Delta H_f°[CaO(s)] + \Delta H_f°[CO_2(g)] - \Delta H_f°[CaCO_3(s)]$

$= (-635.1 - 393.5 - (-1207))\text{kJ} = +178 \text{ kJ}$

heat $= 1.35 \times 10^3 \text{ kg CaCO}_3 \times \dfrac{1000 \text{ g}}{1 \text{ kg}} \times \dfrac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} \times \dfrac{178 \text{ kJ}}{1 \text{ mol CaCO}_3} = 2.40 \times 10^6 \text{ kJ}$

92. **(M)** First we determine the heat of combustion: $\quad C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

$\Delta H° = 4\Delta H_f°[CO_2(g)] + 5\Delta H_f°[H_2O(l)] - \Delta H_f°[C_4H_{10}(g)] - \frac{13}{2}\Delta H_f°[O_2(g)]$

$= (4(-393.5) + 5(-285.8) - (-125.6) - 6.5(0.00))\text{kJ} = -2877.4 \text{ kJ/mol}$

Now compute the volume of gas needed, with the ideal gas equation, rearranged to: $V = \dfrac{nRT}{P}$.

$\text{volume} = \dfrac{\left(5.00 \times 10^4 \text{ kJ} \times \dfrac{1 \text{ mol C}_4\text{H}_{10}}{2877.3 \text{ kJ}}\right) 0.08206 \dfrac{\text{L atm}}{\text{mol K}} (24.6 + 273.2)\text{K}}{756 \text{ mmHg} \times \dfrac{1 \text{ atm}}{760 \text{ mmHg}}} = 427 \text{ L CH}_4$

93. **(M)** The reaction for the combustion of formic acid is:

HCOOH(s) + ½ O_2(g) → CO_2(g) + H_2O(l)
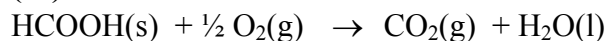
$$\Delta H° = \Delta H_f°\left[CO_2(g)\right] + \Delta H_f°\left[H_2O(1)\right] - \Delta H_f°\left[HCOOH(s)\right] - \tfrac{1}{2}\Delta H_f°\left[O_2(g)\right]$$

$$-255 \text{ kJ} = \left(1(-393.5) + 1(-285.8) - \Delta H_f°\left[HCOOH(s)\right] - 0.5(0.00)\right)\text{kJ}$$

$$-424 \text{ kJ} = \Delta H_f°\left[HCOOH(s)\right]$$

94. **(M)** The reaction for the combustion of lactic acid is:

$C_3H_6O_3$(s) + 3 O_2(g) → 3 CO_2(g) + 3 H_2O(l)
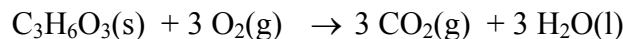
$$\Delta H° = 3\Delta H_f°\left[CO_2(g)\right] + 3\Delta H_f°\left[H_2O(1)\right] - \Delta H_f°\left[C_3H_6O_3(s)\right] - 3\Delta H_f°\left[O_2(g)\right]$$

$$= \left(3(-393.5) + 3(-285.8) - (-694) - 3(0.00)\right)\text{kJ}$$

$$= -1344 \text{ kJ per mole of lactic acid}$$

INTEGRATIVE AND ADVANCED EXERCISES

95. **(M)**

(a) $\text{mass } H_2O = 40 \text{ gal} \times \dfrac{4 \text{ qt}}{1 \text{ gal}} \times \dfrac{1 \text{ L}}{1.06 \text{ qt}} \times \dfrac{1000 \text{ mL}}{1 \text{ L}} \times \dfrac{1.00 \text{ g}}{1 \text{ mL}} \times \dfrac{1 \text{ kg}}{1000 \text{ g}} \times \dfrac{2.205 \text{ lb}}{1 \text{ kg}} = 3.3 \times 10^2 \text{ lb}$

$\text{heat (Btu)} = 3.3 \times 10^2 \text{lb} \times \dfrac{1 \text{ Btu}}{\text{lb °F}} \times (145°F - 48°F) = 3.2 \times 10^4 \text{Btu}$

(b) $\text{heat (kcal)} = 1.5 \times 10^5 \text{ g} \times \dfrac{1 \text{ cal}}{\text{g °C}} \times (145°F - 48°F) \times \dfrac{5 \text{ C°}}{9 \text{ F°}} \times \dfrac{1 \text{ kcal}}{1000 \text{ cal}} = 8.1 \times 10^3 \text{ kcal}$

(c) $\text{heat (kJ)} = 8.1 \times 10^3 \text{ kcal} \times \dfrac{4.184 \text{ kJ}}{1 \text{ kcal}} = 3.4 \times 10^4 \text{ kJ}$

96. **(M)** Potential energy = mgh = 7.26 kg × 9.81 ms^{-2} × 168 m = 1.20 × 10^4 J. This potential energy is converted entirely into kinetic energy just before the object hits, and this kinetic energy is converted entirely into heat when the object strikes.

$$\Delta t = \dfrac{\text{heat}}{\text{mass} \times \text{sp. ht.}} = \dfrac{1.20 \times 10^4 \text{ J}}{7.26 \text{ kg} \times \dfrac{1000 \text{ g}}{1 \text{ kg}} \times \dfrac{0.47 \text{ J}}{\text{g °C}}} = 3.5 °C$$

This large a temperature rise is unlikely, as some of the kinetic energy will be converted into forms other than heat, such as sound and the fracturing of the object along with the surface it strikes. In addition, some heat energy would be transferred to the surface.

97. (M) $\text{heat} = \Delta t \left[\text{heat cap.} + (\text{mass H}_2\text{O} \times 4.184 \ \dfrac{\text{J}}{\text{g}\,^\circ\text{C}})\right]$

$\text{heat cap.} = \dfrac{\text{heat}}{\Delta t} - (\text{mass H}_2\text{O} \times 4.184 \ \dfrac{\text{J}}{\text{g}\,^\circ\text{C}})$

The heat of combustion of anthracene is -7067 kJ/mol, meaning that burning one mole of anthracene releases $+7067$ kJ of heat to the calorimeter.

$\text{heat cap.} = \dfrac{1.354 \text{ g C}_{14}\text{H}_{10} \times \dfrac{1 \text{ mol C}_{14}\text{H}_{10}}{178.23 \text{ g C}_{14}\text{H}_{10}} \times \dfrac{7067 \text{ kJ}}{1 \text{ mol C}_{14}\text{H}_{10}}}{(35.63 \text{ - } 24.87)\,^\circ\text{C}} - \left(983.5 \text{ g} \times 4.184 \times 10^{-3}\ \dfrac{\text{kJ}}{\text{g}\,^\circ\text{C}}\right)$

$= (4.990 - 4.115) \text{ kJ/}^\circ\text{C} = 0.875 \text{ kJ/}^\circ\text{C}$

$\text{heat} = (27.19 - 25.01)\,^\circ\text{C}\,[0.875 \text{ kJ/}^\circ\text{C} + (968.6 \text{ g H}_2\text{O} \times 4.184 \times 10^{-3} \text{ kJ g}^{-1}\,^\circ\text{C}^{-1})] = 10.7 \text{ kJ}$

$q_{rxn} = \dfrac{-10.7 \text{ kJ}}{1.053 \text{ g C}_6\text{H}_8\text{O}_7} \times \dfrac{192.1 \text{ g C}_6\text{H}_8\text{O}_7}{1 \text{ mol C}_6\text{H}_8\text{O}_7} = -1.95 \times 10^3 \text{ kJ/mol C}_6\text{H}_8\text{O}_7$

98. (M) heat absorbed by calorimeter and water $= -$heat of reaction

$= -1.148 \text{ g C}_7\text{H}_6\text{O}_2 \times \dfrac{-26.42 \text{ kJ}}{1 \text{ g C}_7\text{H}_6\text{O}_2} \times \dfrac{1000 \text{ J}}{1 \text{kJ}} = 3.033 \times 10^4 \text{ J}$

heat absorbed by water $= 1181 \text{ g H}_2\text{O} \times \dfrac{4.184 \text{ J}}{\text{g}\,^\circ\text{C}} \times (30.25\,^\circ\text{C} - 24.96\,^\circ\text{C}) = 2.61 \times 10^4 \text{ J}$

heat absorbed by calorimeter $= 3.033 \times 10^4 \text{ J} - 2.61 \times 10^4 \text{ J} = 4.2 \times 10^3 \text{ J}$

heat capacity of the calorimeter $= \dfrac{4.2 \times 10^3 \text{ J}}{30.25\,^\circ\text{C} - 24.96\,^\circ\text{C}} = 7.9 \times 10^2 \text{ J/}^\circ\text{C}$

heat absorbed by water $= 1162 \text{ g H}_2\text{O} \times \dfrac{4.184 \text{ J}}{\text{g}\,^\circ\text{C}} \times (29.81\,^\circ\text{C} - 24.98\,^\circ\text{C}) = 2.35 \times 10^4 \text{ J}$

heat absorbed by calorimeter $= 7.9 \times 10^2 \text{ J/}^\circ\text{C} \times (29.81\,^\circ\text{C} - 24.98\,^\circ\text{C}) = 3.8 \times 10^3 \text{ J}$

heat of combustion $= \dfrac{2.35 \times 10^4 \text{ J} + 3.8 \times 10^3 \text{ J}}{0.895 \text{ g}} \times \dfrac{1 \text{kJ}}{1000 \text{ J}} = 30.5 \text{ kJ/g}$

mass coal $= 2.15 \times 10^9 \text{ kJ} \times \dfrac{1 \text{ g coal}}{30.5 \text{ kJ}} \times \dfrac{1 \text{kg}}{1000 \text{ g}} \times \dfrac{1 \text{ metric ton}}{1000 \text{ kg}} = 70.5 \text{ metric tons}$

99. (M) The difference is due to the enthalpy of vaporization of water. Less heat is evolved when steam is formed because some of the heat of combustion is used to vaporize the water. The difference between these two heats of vaporization is computed first.

$\text{difference} = (33.88 - 28.67)\dfrac{\text{kcal}}{\text{g H}_2} \times \dfrac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} \times \dfrac{2 \text{ mol H}_2}{2 \text{ mol H}_2\text{O}} \times \dfrac{4.184 \text{ kJ}}{1 \text{ kcal}} = 43.9 \text{ kJ/mol H}_2\text{O}$

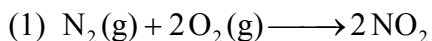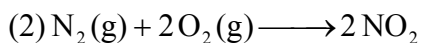This difference should equal the heat of vaporization, that is, the enthalpy change for the following reaction.
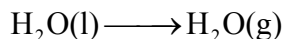
$H_2O(l) \longrightarrow H_2O(g)$ We use values from Table 7-2.

$\Delta H°_{rxn} = \Delta H°_f[H_2O(g)] - \Delta H°_f[H_2O(l)] = -241.8 \, kJ - (-285.8 \, kJ) = 44.0 \, kJ/mol$

The two values are in good agreement.

100. (M)

(1) $N_2(g) + 2O_2(g) \longrightarrow 2NO_2$ $\Delta H°_{rxn} = 2\Delta H°_f[NO_2(g)] = 2 \times 33.18 \, kJ = 66.36 \, kJ$

(2) $N_2(g) + 2O_2(g) \longrightarrow 2NO_2$ $\Delta H = 66.36 \, kJ$

$\underline{2 \ NO_2(g) \longrightarrow N_2O_3(g) + \tfrac{1}{2}O_2(g) \quad\quad\quad\quad \Delta H = 16.02 \, kJ}$

$N_2(g) + 2 \ O_2(g) \longrightarrow N_2O_3(g) + \tfrac{1}{2}O_2(g) \quad \Delta H = 82.38 \, kJ$
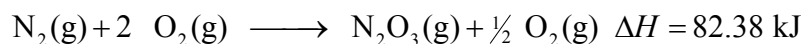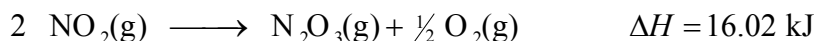
101. (M) First we determine the moles of gas, then the heat produced by burning each of the components.

$$n = \frac{PV}{RT} = \frac{739 \, mm \, Hg \times \dfrac{1 \, atm}{760 \, mmHg} \times 385 \, L}{(22.6 + 273.2)K \times 0.08206 \, L \, atm \, mol^{-1} \, K^{-1}} = 15.4 \, mol$$

$CH_4 \text{ heat} = 15.4 \, mol \times \dfrac{83.0 \ mol \, CH_4}{100.0 \ mol \, gas} \times \dfrac{-890.3 \, kJ}{1 \, mol \, CH_4} = -1.14 \times 10^4 \, kJ$

$C_2H_6 \text{ heat} = 15.4 \, mol \times \dfrac{11.2 \ mol \, C_2H_6}{100.0 \ mol \, gas} \times \dfrac{-1559.7 \, kJ}{1 \, mol \, C_2H_6} = -2.69 \times 10^3 \, kJ$

$C_3H_8 \text{ heat} = 15.4 \, mol \times \dfrac{5.8 \ mol \, C_3H_8}{100.0 \ mol \, gas} \times \dfrac{-2219.1 \, kJ}{1 \, mol \, C_3H_8} = -2.0 \times 10^3 \, kJ$

total heat $= -1.14 \times 10^4 \, kJ - 2.69 \times 10^3 \, kJ - 2.0 \times 10^3 \, kJ = -1.61 \times 10^4 \, kJ$ or $+1.61 \times 10^4 \, kJ$ heat evolved

102. (M)

$CO(g) + 3H_2(g) \longrightarrow CH_4(g) + H_2O(g)$ (methanation)

$2C(s) + 2H_2O(g) \longrightarrow 2CO(g) + 2H_2(g)$ $2 \times (7.24)$

$\underline{CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g) \quad\quad\quad\quad (7.25)}$

$2C(s) + 2H_2O(g) \longrightarrow CH_4(g) + CO_2(g)$
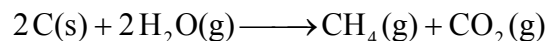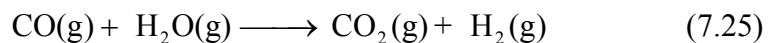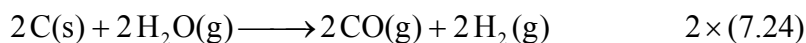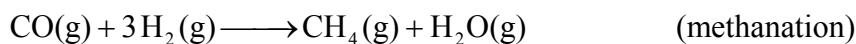
103. (D)   We first compute the heats of combustion of the combustible gases.

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

    $\Delta H°_{rxn} = \Delta H°_f[CO_2(g)] + 2\Delta H°_f[H_2O(l)] - \Delta H°_f[CH_4(g)] - 2\Delta H°_f[O_2(g)]$

       $= -393.5 \, kJ + 2 \times (-285.8 \, kJ) - (-74.81 \, kJ) - 2 \times 0.00 \, kJ = -890.3 \, kJ$

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$
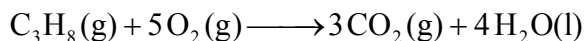
$\quad \Delta H°_{rxn} = 3\Delta H°_f[CO_2(g)] + 4\Delta H°_f[H_2O(l)] - \Delta H°_f[C_3H_8(g)] - 5\Delta H°_f[O_2(g)]$

$\quad\quad = 3\times(-393.5\,kJ) + 4\times(-285.8\,kJ) - (-103.8\,kJ) - 5\times0.00\,kJ = -2220.\,kJ$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H°_{rxn} = \Delta H°_f[H_2O(l)] = -285.8\,kJ$

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$
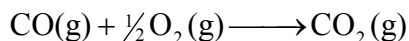
$\Delta H°_{rxn} = \Delta H°_f[CO_2(g)] - \Delta H°_f[CO(g)] - 0.5\Delta H°_f[O_2(g)] = -393.5 + 110.5 = -283.0\,kJ$

Then, for each gaseous mixture, we compute the enthalpy of combustion per mole of gas. The enthalpy of combustion per STP liter is 1/22.414 of this value. Recall that volume percents are equal to mole percents.

(a) H_2 combustion $= 0.497\,mol\,H_2 \times \dfrac{-285.8\,kJ}{1\,mol\,H_2} = -142\,kJ$

$\quad CH_4$ combustion $= 0.299\,mol\,CH_4 \times \dfrac{-890.3\,kJ}{1\,mol\,CH_4} = -266\,kJ$

$\quad CO$ combustion $= 0.069\,mol\,CO \times \dfrac{-283.0\,kJ}{1\,mol\,CO} = -20\,kJ$

$\quad C_3H_8$ combustion $= 0.031\,mol\,C_3H_8 \times \dfrac{-2220.\,kJ}{1\,mol\,C_3H_8} = -69\,kJ$

$\quad$ total enthalpy of combustion $= \dfrac{(-142 - 266 - 20 - 69)\,kJ}{1\,mol\,gas} \times \dfrac{1\,mol\,gas}{22.414\,L\,STP} = -22.2\,kJ/L$

(b) CH_4 is the only combustible gas present in sewage gas.

$\quad$ total enthalpy of combustion $= 0.660\,mol\,CH_4 \times \dfrac{-890.3\,kJ}{1\,mol\,CH_4} \times \dfrac{1\,mol\,gas}{22.414\,L\,STP} = -26.2\,kJ/L$

Thus, sewage gas produces more heat per liter at STP than does coal gas.

104.(M)

(a) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ is the combustion reaction

$\quad \Delta H°_{rxn} = \Delta H°_f[CO_2(g)] + 2\Delta H°_f[H_2O(l)] - \Delta H°_f[CH_4(g)] - 2\Delta H°_f[O_2(g)]$

$\quad\quad = (-393.5\,kJ) + 2\times(-285.8\,kJ) - (-74.81\,kJ) - 2\times0.00\,kJ = -890.3\,kJ$

$n = \dfrac{PV}{RT} = \dfrac{744\,mm\,Hg \times \dfrac{1\,atm}{760\,mmHg} \times 0.100\,L}{298.2\,K \times 0.08206\,L\,atm\,mol^{-1}\,K^{-1}} = 0.00400\,mol\,CH_4$

heat available from combustion $= 0.00400\,mol \times$ -890.3 kJ/mol $=$ -3.56 kJ

heat used to melt ice $= 9.53\,g\,ice \times \dfrac{1\,mole\,H_2O(s)}{18.02\,g\,ice} \times \dfrac{6.01\,kJ}{1\,mol\,H_2O(s)} = 3.18\,kJ$

Since 3.56 kJ of heat was available, and only 3.18 kJ went into melting the ice, the combustion   must be incomplete.

(b) One possible reaction is: $4CH_4(g) + 7O_2(g) \longrightarrow 2\ CO_2(g) + 2CO(g) + 8H_2O(l)$, but this would generate but 3.00 kJ of energy under the stated conditions. The molar production of CO_2 (g) must be somewhat greater than that of CO(g).

105. (E)

(a) The heat of reaction would be smaller (less negative) if the H_2O were obtained as a gas rather than as a liquid.

(b) The reason why the heat of reaction would be less negative is that some of the 1410.9 kJ of heat produced by the reaction will be needed to convert the H_2O from liquid to gas.

(c)
$$\Delta H° = 2\Delta H°_f[CO_2(g)] + 2\Delta H°_f[H_2O(g)] - \Delta H°_f[C_2H_4(g)] - 3\Delta H°_f[O_2(g)]$$
$$= 2(-393.5) + 2(-241.8) - (52.26) - 3(0.00) = -1322.9\,kJ$$

106. (D) First we compute the amount of butane in the cylinder before and after some is withdrawn; the difference is the amount of butane withdrawn.
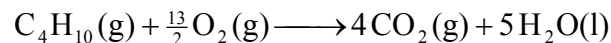T = (26.0 + 273.2)K = 299.2 K

$$n_1 = \frac{PV}{RT} = \frac{2.35\,atm \times 200.0\,L}{0.08206\,L\,atm\,mol^{-1}\,K^{-1} \times 299.2\,K} = 19.1\,mol\,butane$$

$$n_2 = \frac{PV}{RT} = \frac{1.10\,atm \times 200.0\,L}{0.08206\,L\,atm\,mol^{-1}\,K^{-1} \times 299.2\,K} = 8.96\,mol\,butane$$

amount withdrawn $= 19.1\,mol - 8.96\,mol = 10.1\,mol\,butane$
Then we compute the enthalpy change for one mole of butane and from that the heat produced by burning the withdrawn butane.

$$C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$$

$$\Delta H°_{rxn} = 4\Delta H°_f[CO_2(g)] + 5\Delta H°_f[H_2O(l)] - \Delta H°_f[C_4H_{10}(g)] - \tfrac{13}{2}\Delta H°_f[O_2(g)]$$
$$= 4 \times (-393.5\,kJ) + 5 \times (-285.8\,kJ) - (-125.6\,kJ) - 6.5 \times 0.00\,kJ = -2877\ kJ$$

Now we compute the heat produced by the combustion of the butane.

$$heat = 10.1\,mol\,C_4H_{10} \times \frac{-2877\,kJ}{1\,mol\,C_4H_{10}} = -2.91 \times 10^4\ kJ$$

To begin the calculation of the heat absorbed by the water, we compute the mass of the water.

$$\text{mass H}_2\text{O} = 132.5\,\text{L} \times \frac{1000\,\text{cm}^3}{1\,\text{L}} \times \frac{1.00\,\text{g}}{1\,\text{cm}^3} = 1.33 \times 10^5\,\text{g H}_2\text{O}$$

$$\text{heat absorbed} = 1.33 \times 10^5\,\text{g} \times \frac{4.184\,\text{J}}{\text{g}\,^\circ\text{C}} \times (62.2\,^\circ\text{C} - 26.0\,^\circ\text{C}) \times \frac{1\,\text{kJ}}{1000\,\text{J}} = 2.01 \times 10^4\,\text{kJ}$$

$$\%\,\text{efficiency} = \frac{2.01 \times 10^4\,\text{kJ absorbed}}{2.91 \times 10^4\,\text{kJ produced}} \times 100\% = 69.1\%\,\text{efficient}$$

107. (M) $\text{work} = 4 \times mgh = 4 \times 58.0\,\text{kg} \times 9.807\,\text{m}\,\text{s}^{-2} \times 1450\,\text{m} \times \dfrac{1\,\text{kJ}}{1000\,\text{J}} = 3.30 \times 10^3\,\text{kJ}$

We compute the enthalpy change for the metabolism (combustion) of glucose.
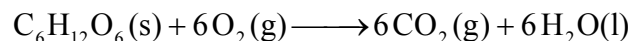
$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l)$$
$$\Delta H^\circ_{\text{rxn}} = 6\,\Delta H^\circ_f[CO_2(g)] + 6\,\Delta H^\circ_f[H_2O(l)] - \Delta H^\circ_f[C_6H_{12}O_6(s)] - 6\,\Delta H^\circ_f[O_2(g)]$$
$$= 6 \times (-393.5\,\text{kJ}) - 6 \times (-285.8\,\text{kJ}) - (-1273.3\,\text{kJ}) - 6 \times 0.00\,\text{kJ} = -2802.5\,\text{kJ}$$

Then we compute the mass of glucose needed to perform the necessary work.

$$\text{mass } C_6H_{12}O_6 = 3.30 \times 10^3\,\text{kJ} \times \frac{1\,\text{kJ heat}}{0.70\,\text{kJ work}} \times \frac{1\,\text{mol }C_6H_{12}O_6}{2802.5\,\text{kJ}} \times \frac{180.2\,\text{g }C_6H_{12}O_6}{1\,\text{mol }C_6H_{12}O_6}$$

$$= 303\,\text{g } C_6H_{12}O_6$$

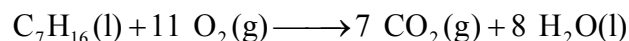**108.(M)** $\Delta H^\circ_f[C_4H_{10}(g)] = -125.6\,\text{kJ/mol}$ from Table 7-2.

The difference between C_4H_{10} and C_7H_{16} amounts to three CH_2 groups. The difference in their standard enthalpies of formation is determined as follows.

$$\text{difference} = 3\,\text{mol CH}_2\text{ groups} \times \frac{-21\,\text{kJ}}{\text{mol CH}_2\text{ groups}} = -63\,\text{kJ/mol}$$
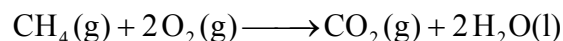
Thus $\quad \Delta H^\circ_f[C_7H_{16}(l)] \approx -125.6\,\text{kJ/mol} - 63\,\text{kJ/mol} = -189\,\text{kJ/mol}$

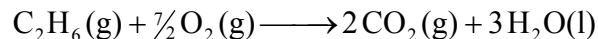Now we compute the enthalpy change for the combustion of heptane.

$$C_7H_{16}(l) + 11\,O_2(g) \longrightarrow 7\,CO_2(g) + 8\,H_2O(l)$$
$$\Delta H^\circ_{\text{rxn}} = 7\,\Delta H^\circ_f[CO_2(g)] + 8\,\Delta H^\circ_f[H_2O(l)] - \Delta H^\circ_f[C_7H_{16}(l)] - 11\,\Delta H^\circ_f[O_2(g)]$$
$$= 7 \times (-393.5\,\text{kJ}) + 8 \times (-285.8\,\text{kJ}) - (-189\,\text{kJ}) - 11 \times 0.00\,\text{kJ} = -4852\,\text{kJ}$$

109. (M) First determine the molar heats of combustion for CH_4 and C_2H_6.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$$
$$\Delta H^\circ = \Delta H^\circ_f[CO_2(g)] + 2\,\Delta H^\circ_f[H_2O(l)] - \Delta H^\circ_f[CH_4(g)] - 2\,\Delta H^\circ_f[O_2(g)]$$
$$= \big((-393.5) + 2(-285.8) - (-74.81) - 2(0.00)\big)\,\text{kJ} = -890.3\,\text{kJ/mol}$$

$$C_2H_6(g) + \tfrac{7}{2}\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$$

$$\Delta H^\circ = 2\,\Delta H^\circ{}_f[CO_2\,(g)] + 3\,\Delta H^\circ{}_f[H_2O(l)] - \Delta H^\circ{}_f[C_2H_6\,(g)] - \tfrac{7}{2}\,\Delta H^\circ{}_f[O_2\,(g)]$$

$$= \big(2(-393.5) + 3(-285.8) - (-84.68) - \tfrac{7}{2}(0.00)\big)\,kJ = -1559.7\,kJ$$

Since the STP molar volume of an ideal gas is 22.4 L, there is 1/22.4 of a mole of gas present in the sample. We first compute the heat produced by one mole (that is 22.4 L at STP) of the mixed gas.

$$heat = \frac{43.6\,kJ}{1.00\,L} \times \frac{22.4\,L}{1\,mol} = 977\,kJ/mol$$

Then, if we let the number of moles of CH_4 be represented by x, the number of moles of C_2H_6 is represented by $(1.00 - x)$. Now we can construct an equation for the heat evolved per mole of mixture and solve this equation for x.
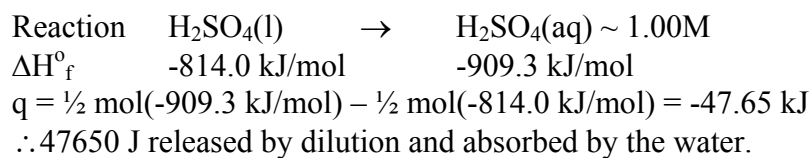
$$977\,kJ = 890.3\,x + 1559.7(1.00 - x) = 1559.7 + (890.3 - 1559.7)x = 1559.7 - 669.4\,x$$

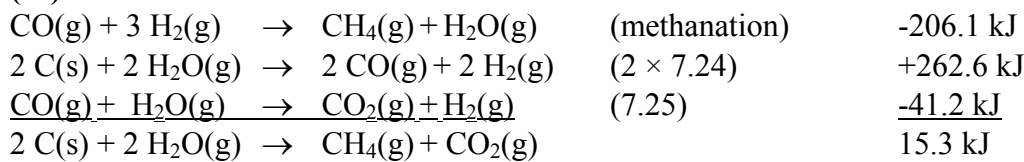$$x = \frac{1559.7 - 977}{669.4} = 0.870\,mol\,CH_4/mol\,mixture$$

By the ideal gas law, gases at the same temperature and pressure have the same volume ratio as their molar ratio. Hence, this gas mixture contains 87.0% CH_4 and 13.0% C_2H_6, both by volume.

110. **(D)**

    (a) Values are not the same because enthalpies of formations in solution depend on the solute concentration.

    (b) The data that we can cite to confirm that the $\Delta H^\circ{}_f[H_2SO_4(aq)]$ = -909.3 kJ/mol in an infinitely dilute solution is the same for the $\Delta H^\circ{}_f[SO_4^{2-}]$ from Table 7.3. This is expected because an infinitely dilute solution of H_2SO_4 is 2 $H^+(aq)$ + $SO_4^{2-}(aq)$. Since $\Delta H^\circ{}_f[H^+]$ = 0 kJ/mol, it is expected that $SO_4^{2-}(aq)$ will have the same $\Delta H^\circ{}_f$ as $H_2SO_4(aq)$.

    (c) 500.0 mL of 1.00 M H_2SO_4 is prepared from pure H_2SO_4. Note: ½ mole H_2SO_4 used.

        Reaction $H_2SO_4(l)$ $\rightarrow$ $H_2SO_4(aq) \sim 1.00M$
        $\Delta H^\circ{}_f$ -814.0 kJ/mol   -909.3 kJ/mol
        q = ½ mol(-909.3 kJ/mol) – ½ mol(-814.0 kJ/mol) = -47.65 kJ
        $\therefore$ 47650 J released by dilution and absorbed by the water.

        Use q = mcΔt $\Delta t = \dfrac{47650\,J}{500\,g(4.2\,J\,g^{-1}\,°C^{-1})} \approx +23\,°C$

111. **(M)**

$CO(g) + 3\,H_2(g)$	$\rightarrow$	$CH_4(g) + H_2O(g)$	(methanation)	-206.1 kJ
$2\,C(s) + 2\,H_2O(g)$	$\rightarrow$	$2\,CO(g) + 2\,H_2(g)$	(2 × 7.24)	+262.6 kJ
$\underline{CO(g) + H_2O(g)}$	$\underline{\rightarrow}$	$\underline{CO_2(g) + H_2(g)}$	(7.25)	-41.2 kJ
$2\,C(s) + 2\,H_2O(g)$	$\rightarrow$	$CH_4(g) + CO_2(g)$		15.3 kJ

112. (M)

$$n = \frac{(765.5/760)\text{atm}}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})}\frac{0.582\text{L}}{298.15\text{K}} = 2.40\times10^{-2}\text{mol}$$

$$\text{molar mass} = \frac{1.103\text{g}}{2.40\times10^{-2}\text{mol}} = 46.0 \text{ g/mol}$$

moles of CO_2 = 2.108/44.01 = 0.04790 (0.0479 mol C in unknown)

moles of H_2O = 1.294/18.02 = 0.0719 (0.144 mol H in unknown)

$$\text{moles of O in unknown} = \frac{1.103 \text{ g - 0.04790 g (12.011g C/mol)-0.144(1.00794)}}{15.9994 \text{ g mol}^{-1}} = 0.0239 \text{ mol O}$$

So C:H:O ratio is 2:6:1 and the molecular formula is C_2H_6O.

ΔT = 31.94 - 25.00 = 6.94 °C $\qquad$ q = 6.94 °C × 5.015kJ/°C = −34.8kJ

$$\Delta H = \frac{-34.8\text{kJ}}{0.0240\text{mol}} = -1.45\times10^3\text{kJ/mol} \qquad 3\ O_2(g)\ +\ C_2H_6O(g) \rightarrow 2\ CO_2(g)+\ 3\ H_2O(l)$$

113. (M) Energy needed = mcΔT = (250 g)((50-4) °C)(4.2J/g °C) = 4.8×10^4 J
A 700-watt oven delivers a joule of energy/sec.

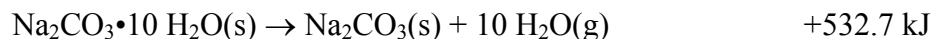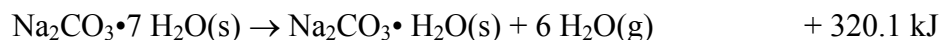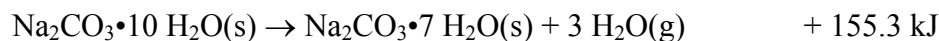$$\text{time} = \left(\frac{4.8\times10^4 \text{ J}}{700 \text{ J sec}^{-1}}\right) = 69 \text{ seconds}$$

114. (M) w = -PΔV, V_i = (3.1416)(6.00 cm)^2(8.10 cm) = 916.1 cm^3

$$P = \frac{\text{force}}{\text{area}} = \frac{(3.1416)(5.00)^2(25.00)(7.75\text{g/cm}^3)(1\text{kg/1000g})(9.807\text{m/sec}^2)}{(3.1416)(6.00 \text{ cm})^2(1\text{m/100cm})^2}$$

$$= 1.320\times10^4 \text{ Pa} = \frac{1.320\times10^4 \text{ Pa}}{101325 \text{ Pa atm}^{-1}} = 0.130 \text{ atm difference} \qquad \text{Use: } P_1V_1 = P_2V_2$$

$$V_2 = \frac{((745/760) + 0.130\text{atm})\times(0.9161\text{L})}{(745/760)\text{atm}} = 1.04 \text{ L}$$

$$-\text{P}\Delta\text{V} = \frac{745}{760}\times(1.04-0.916) = -0.121 \text{ L} - \text{atm} = w = (-0.121 \text{ L} - \text{atm})\frac{101 \text{ J}}{\text{L}-\text{atm}} = -12 \text{ J}$$

115. (M)

$Na_2CO_3 \cdot 10\ H_2O(s) \rightarrow Na_2CO_3 \cdot 7\ H_2O(s) + 3\ H_2O(g)$	+ 155.3 kJ
$Na_2CO_3 \cdot 7\ H_2O(s) \rightarrow Na_2CO_3 \cdot H_2O(s) + 6\ H_2O(g)$	+ 320.1 kJ
$\underline{Na_2CO_3 \cdot H_2O(s) \rightarrow Na_2CO_3(s) + H_2O(g)}$	$\underline{+\ 57.3 \text{ kJ}}$
$Na_2CO_3 \cdot 10\ H_2O(s) \rightarrow Na_2CO_3(s) + 10\ H_2O(g)$	+532.7 kJ

Thus, using Hess's Law, ΔH = +532.7 kJ. For ΔU we must assume a temperature, say, 373 K.
$\Delta U = \Delta H -\Delta n_{gas}RT$ = +532.7 kJ – 10 mol(8.314472 J K^{-1} mol^{-1})(373 L)(1 kJ/1000 J) = +501.7 kJ
The value for ΔU is only an estimate because it is based on a ΔH value that has been obtained using Hess's law. Hess's law provides only an approximate value for the enthalpy change. To

obtain a more precise value for the ΔU, one would use bomb calorimetry. As well, the water formed is assumed to be a vapor (gas). In reality, a portion of that water will exist as a liquid.
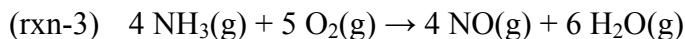
116. **(M)** First, list all of the pertinent reactions, normalizing them so that each uses the same amount of NH_3:
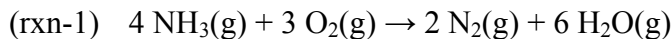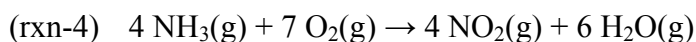
(rxn-1) $4 NH_3(g) + 3 O_2(g) \rightarrow 2 N_2(g) + 6 H_2O(g)$
$\Delta H°_{rxn-1} = 2\times(0 \text{ kJ/mol}) + 6\times(-241.8 \text{ kJ/mol}) - [4\times(-46.11 \text{ kJ}) + 3\times(0 \text{ kJ/mol})] = -1266.4 \text{ kJ}$
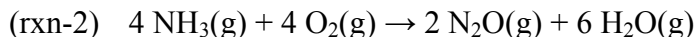
(rxn-2) $4 NH_3(g) + 4 O_2(g) \rightarrow 2 N_2O(g) + 6 H_2O(g)$
$\Delta H°_{rxn-2} = 4\times(82.05 \text{ kJ/mol}) + 6\times(-241.8 \text{ kJ/mol}) - [4\times(-46.11 \text{ kJ}) + 3\times(0 \text{ kJ/mol})] = -938.2 \text{ kJ}$

(rxn-3) $4 NH_3(g) + 5 O_2(g) \rightarrow 4 NO(g) + 6 H_2O(g)$
$\Delta H°_{rxn-3} = 2\times(90.25 \text{ kJ/mol}) + 6\times(-241.8 \text{ kJ/mol}) - [4\times(-46.11 \text{ kJ}) + 3\times(0 \text{ kJ/mol})] = -1085.9 \text{ kJ}$

(rxn-4) $4 NH_3(g) + 7 O_2(g) \rightarrow 4 NO_2(g) + 6 H_2O(g)$
$\Delta H°_{rxn-4} = 4\times(33.18 \text{ kJ/mol}) + 6\times(-241.8 \text{ kJ/mol}) - [4\times(-46.11 \text{ kJ}) + 3\times(0 \text{ kJ/mol})] = -1133.6 \text{ kJ}$

Clearly, rxn-1, the oxidation of $NH_3(g)$ to $N_2(g)$ is the most exothermic reaction.

117. **(D)**
$$\Delta H = \int_{298 \text{ K}}^{373 \text{ K}} C_p dt = \int_{298 \text{ K}}^{373 \text{ K}} (28.58 + 0.00377T - 0.5\times10^5 T^{-2}) dt$$

$$\Delta H = 28.58 \frac{J}{K \text{ mol}} \int_{298K}^{373 \text{ K}} dt + 0.00377 \frac{J}{K^2 \text{ mol}} \int_{298K}^{373 \text{ K}} T dt + -0.5\times10^5 \frac{J K}{mol} \int_{298K}^{373 \text{ K}} T^{-2} dt$$

$$\Delta H = 28.58 \frac{J}{K \text{ mol}} \times \left(T\Big|_{298 \text{ K}}^{373 \text{ K}}\right) + 0.00377 \frac{J}{K^2 \text{ mol}} \times \left(\frac{T^2}{2}\Big|_{298 \text{ K}}^{373 \text{ K}}\right) - 0.5\times10^5 \frac{J K}{mol} \times \left(-\frac{1}{T}\Big|_{298 \text{ K}}^{373 \text{ K}}\right)$$

$$\Delta H = 28.58 \frac{J}{K \text{ mol}} \times (373 \text{ K} - 298 \text{ K}) + 0.00377 \frac{J}{K^2 \text{ mol}} \times \left(\frac{(373 \text{ K})^2}{2} - \frac{(298 \text{ K})^2}{2}\right)$$

$$+ 0.5\times10^5 \frac{J K}{mol} \times \left(\frac{1}{373 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

$$\Delta H = 2143.5 \frac{J}{mol} + 94.9 \frac{J}{mol} - 33.7 \frac{J}{mol} = 2205 \frac{J}{mol} = 2.205 \frac{kJ}{mol}$$

118.   **(D)** In this problem, there are four distinct heating regimes: (1) heating the ice from -5 ºC to the melting point at 0 ºC, (2) heat required to melt the ice, ΔH_{fus}, (3) heating the water from 0 ºC to the boiling point at 100 ºC, and (4) heat required to vaporize the water, ΔH_{vap}. Each part is solved separately below. However, we must first calculate the temperature dependent heat capacity of ice and water in their given temperature ranges. We also note that melting ice to water at 273 K requires an enthalpy (ΔH_{fus}) of 6.01 kJ/mol, and boiling water requires an enthalpy (ΔH_{vap}) of 44.0 kJ/mol.

$$C_p(ice) = \int_{268K}^{273K} 1.0187 \cdot T - 1.49 \times 10^{-2} = \left[1.0187 \frac{T^2}{2} - 1.49 \times 10^{-2} T \right]_{268}^{273} = 1337.71 \, kJ \cdot kg^{-1} \cdot K^{-1}$$

$$C_p(water) = \int_{273K}^{373K} -1.0 \times 10^{-7} \cdot T^3 + 1.0 \times 10^{-4} \cdot T^2 - 3.92 \times 10^{-2} \cdot T + 8.7854$$

$$= \left[-1.0 \times 10^{-7} \cdot \frac{T^4}{4} + 1.0 \times 10^{-4} \cdot \frac{T^3}{3} - 3.92 \times 10^{-2} \cdot \frac{T^2}{2} + 8.7854 \cdot T \right]_{273}^{373} = 318.95 \, kJ \cdot kg^{-1} \cdot K^{-1}$$

Now we use the above data to determine the q values:

$$q_1(ice, 268K \rightarrow 273K) = (0.010 \, kg)(1337.71 \, kJ \cdot kg^{-1} \cdot K^{-1})(273K - 268K) = 68.89 \, kJ$$

$$q_2(ice \rightarrow water) = 0.010 \, kg \, ice \times \frac{1 \, mol \, H_2O}{0.01801 \, kg} \times \frac{6.01 \, kJ}{mol} = 3.34 \, kJ$$

$$q_3(water, 273K \rightarrow 373K) = (0.010 \, kg)(318.95 \, kJ \cdot kg^{-1} \cdot K^{-1})(373K - 273K) = 318.95 \, kJ \cdot kg^{-1} \cdot K^{-1}$$

$$q_4(water \rightarrow steam) = 0.010 \, kg \, water \times \frac{1 \, mol \, H_2O}{0.01801 \, kg} \times \frac{44.0 \, kJ}{mol} = 24.41 \, kJ$$

$$q_{TOT} = 415.59 \, kJ$$

119. (D) Reaction of interest:

	$H_2(g)$	+	½ $O_2(g)$	→	$H_2O(g)$
Molar heat capacities:	28.84 J K⁻¹mol⁻¹		29.37 J K⁻¹mol⁻¹		33.58 J K⁻¹mol⁻¹

Molar heat capacities: 28.84 J $K^{-1}mol^{-1}$ 29.37 J $K^{-1}mol^{-1}$ 33.58 J $K^{-1}mol^{-1}$

ΔT 75.0 K   75.0 K   75.0 K

$q = n \times C_p \times \Delta T$ (1)(28.84)(75.0) J = 2163 J   (½)(29.37)(75.0) J = 1101.4 J   (1)(33.58)(75.0) J = 2518.5 J

$q_{prod} = 2518.5 \, J = 2.52 \, kJ$ $q_{react} = (2163 \, J + 1101.4 \, J) = 3264.4 \, J = 3.26 \, kJ$

See diagram below.
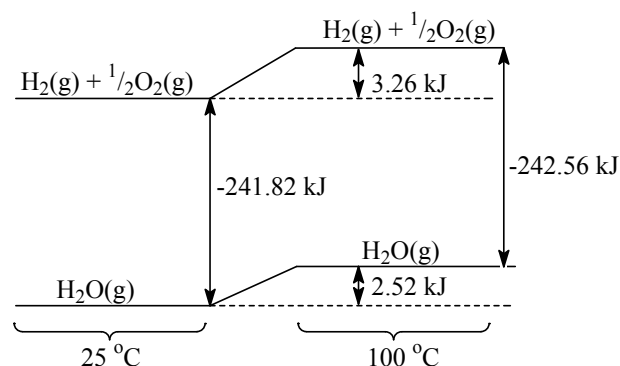
Thus, $\Delta H^\circ_f H_2O(g)$ at 100.0 ° C is approximately -243 kJ/mol $H_2O(g)$ formed.

FEATURE PROBLEMS

120. **(M)** $1\ °F = 5/9\ °C = 0.555\ °C$ $1\ lb = 453.6\ g$

$E_p = mgh$

$E_p = (772\ lb)(9.80665\ m\ s^{-2})(1\ ft) = 7.57 \times 10^3\ \dfrac{lb\ m\ ft}{s^2}$

$E_p = 7.57 \times 10^3\ \dfrac{lb\ m\ ft}{s^2} \times \dfrac{0.3048\ m}{ft} \times \dfrac{0.4536\ kg}{lb}$

$E_p = 1047\ \dfrac{kg\ m^2}{s^2} = 1047\ J = 1.05\ kJ$

The statement is validated.

$q = m \times (sp.\ ht.)\Delta T$

$q = 453.6\ g(4.184\ \dfrac{J}{g\ °C})(0.556\ °C)$

$q = 1054\ J$

$q = 1.05\ kJ$

121. **(D)**

(a)   We plot specific heat vs. the inverse of atomic mass.
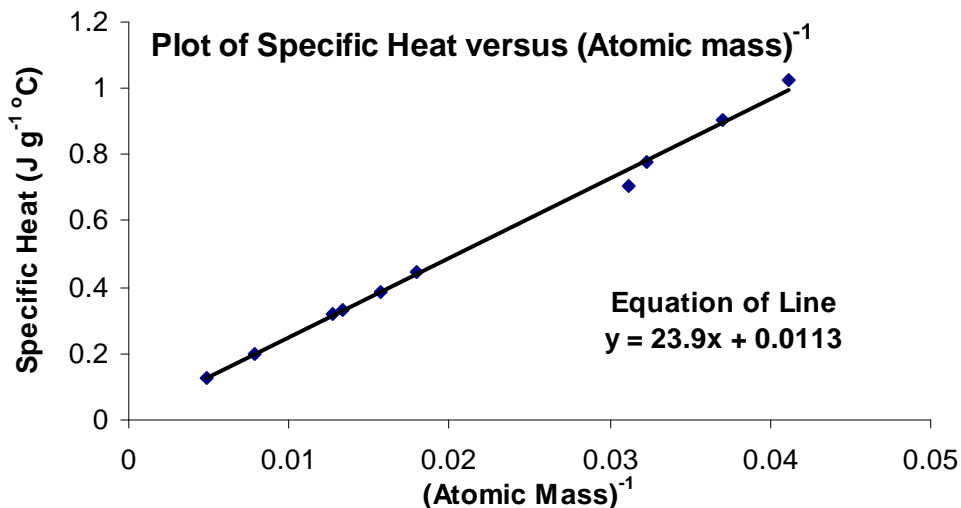
(b)   The equation of the line is: specific heat $= 23.9 \div (\text{atomic mass}) + 0.0113$

$0.23\ J\ g^{-1}\ °C = 23.9 \div (\text{atomic mass}) + 0.0113$

$\text{atomic mass} = \dfrac{23.9}{0.23 - 0.0113} = 10\underline{9}\ u\ \text{or}\ 110\ u\ (2\ \text{sig fig})$;

Cadmium's tabulated atomic mass is 112.4 u.

(c) $sp.ht. = \dfrac{450\ J}{75.0\ g \times 15.\ °C} = 0.40\ J\ g^{-1}\ °C^{-1} = 0.0113 + 23.9/\text{atomic mass}$

$\text{atomic mass} = \dfrac{23.9}{0.40 - 0.0113} = 61.\underline{5}\ u\ \text{or}\ 62\ u$ The metal is most likely $Cu\ (63.5\ u)$.

122. **(D)** The plot's maximum is the equivalence point. (Assume $\Delta T = 0$ at 0 mL of added NaOH, (i.e., only 60 mL of citric acid are present), and that $\Delta T = 0$ at 60 mL of NaOH (i.e. no citric acid added).
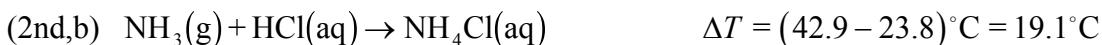

Plot of ΔT versus Volume of NaOH
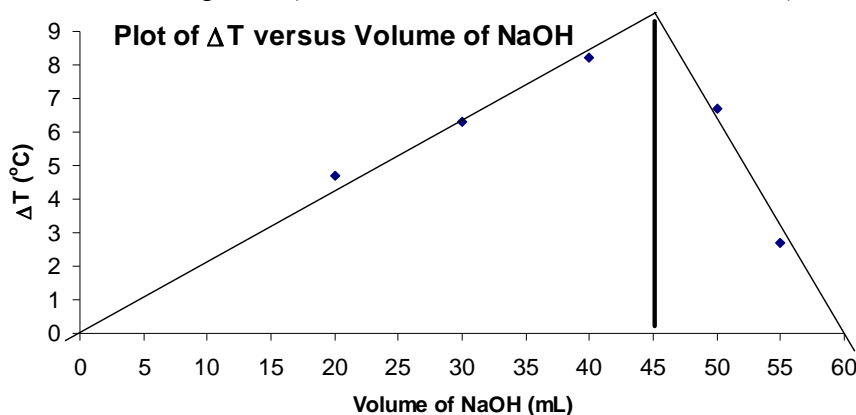
(a)   The equivalence point occurs with 45.0 mL of 1.00 M NaOH(aq) [45.0 mmol NaOH] added and 15.0 mL of 1.00 M citric acid [15.0 mmol citric acid]. Again, we assume that $\Delta T =$ zero if no NaOH added ($V_{NaOH} = 0$ mL) and $\Delta T = 0$ if no citric acid is added ($V_{NaOH} = 60$).

(b)   Heat is a product of the reaction, as are chemical species (products). Products are maximized at the exact stoichiometric proportions. Since each reaction mixture has the same volume, and thus about the same mass to heat, the temperature also is a maximum at this point.

(c) $H_3C_6H_5O_7(s) + 3\,OH^- (aq) \rightarrow 3\,H_2O(l) + C_6H_5O_7{}^{3-}(aq)$

123. **(M)**
(a)   The reactions, and their temperature changes, are as follows.

(1st) $NH_3(\text{conc. aq}) + HCl(aq) \rightarrow NH_4Cl(aq)$ $\Delta T = (35.8 - 23.8)\,°C = 12.0\,°C$

(2nd,a) $NH_3(\text{conc. aq}) \rightarrow NH_3(g)$ $\Delta T = (13.2 - 19.3)\,°C = -6.1\,°C$

(2nd,b) $NH_3(g) + HCl(aq) \rightarrow NH_4Cl(aq)$ $\Delta T = (42.9 - 23.8)\,°C = 19.1\,°C$

The sum of reactions $(2nd, a) + (2nd, b)$ produces the same change as the 1st reaction.

(b)   We now compute the heat absorbed by the surroundings for each. Hess's law is demonstrated if $\Delta H_1 = \Delta H_{2a} + \Delta H_{2b}$, where in each case $\Delta H = -q$.

$q_1 = \left[(100.0 \text{ mL} + 8.00 \text{ mL}) \times 1.00 \text{ g} / \text{mL} \right] 4.18 \text{ J g}^{-1}\,°C^{-1} \times 12.0\,°C = 5.42 \times 10^3 \text{ J} = -\Delta H_1$

$q_{2a} = \left[(100.0 \text{ mL} \times 1.00 \text{ g/mL}) \, 4.18 \text{ J g}^{-1}\,°C^{-1} \times (-6.1\,°C) \right] = -2.55 \times 10^3 \text{ J} = -\Delta H_{2a}$

$q_{2b} = \left[(100.0 \text{ mL} \times 1.00 \text{ g} / \text{mL}) \, 4.18 \text{ J g}^{-1}\,°C^{-1} \times (19.1\,°C) \right] = 7.98 \times 10^3 \text{ J} = -\Delta H_{2b}$

$\Delta H_{2a} + \Delta H_{2b} = +2.55 \times 10^3 \text{ J} - 7.98 \times 10^3 \text{ J} = -5.43 \times 10^3 \text{ J} \cong -5.42 \times 10^3 \text{ J} = \Delta H_1 \,(QED)$

124. **(D)** According to the kinetic-molecular theory of gases, the internal energy of an ideal gas, U, is proportional to the average translational kinetic energy for the gas particles, e_k, which in turn is proportional to 3/2 RT. Thus the internal energy for a fixed amount of an ideal gas depends only on its temperature, i.e., $U = 3/2\ nRT$, where U is the internal energy (J), n is the number of moles of gas particles, R is the gas constant (J K^{-1} mol^{-1}), and T is the temperature (K). If the temperature of the gas sample is changed, the resulting change in internal energy is given by $\Delta U = 3/2\ nR\Delta T$.

(a) At constant volume, $q_v = nC_v\Delta T$. Assuming that no work is done $\Delta U = q_v$ so,
$\Delta U = q_v = 3/2nR\Delta T = nC_v\Delta T$. (divide both sides by $n\Delta T$) $C_v = 3/2$ R= 12.5 J/K·mol.

(b) The heat flow at constant pressure q_p is the ΔH for the process (i.e., $q_p = \Delta H$) and we know that $\Delta H = \Delta U - w$ and $w = -P\Delta V = -nR\Delta T$.
Hence, $q_p = \Delta U - w = \Delta U - (-nR\Delta T) = \Delta U + nR\Delta T$ and $q_p = nC_p\Delta T$ and
$\Delta U = 3/2\ nR\Delta T$ Consequently $q_p = nC_p\Delta T = nR\Delta T + 3/2\ nR\Delta T$ (divide both sides by $n\Delta T$) Now, $C_p = R + 3/2\ R = 5/2\ R = 20.8$ J/K·mol.

125. **(D)**

(a) Here we must determine the volume between 2.40 atm and 1.30 atm using $PV = nRT$

$$V = \frac{0.100\,\text{mol} \times 0.08206\ \dfrac{\text{L atm}}{\text{K mol}} \times 298\ \text{K}}{P} = \frac{2.445\,\text{L atm}}{P}$$

For $P = 2.40$ atm: $V = 1.02$ L
For $P = 2.30$ atm: $V = 1.06$ L $P\Delta V = 2.30$ atm $\times -0.04$ L $= -0.092$ L atm
For $P = 2.20$ atm: $V = 1.11$ L $P\Delta V = 2.20$ atm $\times -0.05$ L $= -0.11$ L atm
For $P = 2.10$ atm: $V = 1.16$ L $P\Delta V = 2.10$ atm $\times -0.05$ L $= -0.11$ L atm
For $P = 2.00$ atm: $V = 1.22$ L $P\Delta V = 2.00$ atm $\times -0.06$ L $= -0.12$ L atm
For $P = 1.90$ atm: $V = 1.29$ L $P\Delta V = 1.90$ atm $\times -0.06$ L $= -0.12$ L atm
For $P = 1.80$ atm: $V = 1.36$ L $P\Delta V = 1.80$ atm $\times -0.07$ L $= -0.13$ L atm
For $P = 1.70$ atm: $V = 1.44$ L $P\Delta V = 1.70$ atm $\times -0.08$ L $= -0.14$ L atm
For $P = 1.60$ atm: $V = 1.53$ L $P\Delta V = 1.60$ atm $\times -0.09$ L $= -0.14$ L atm
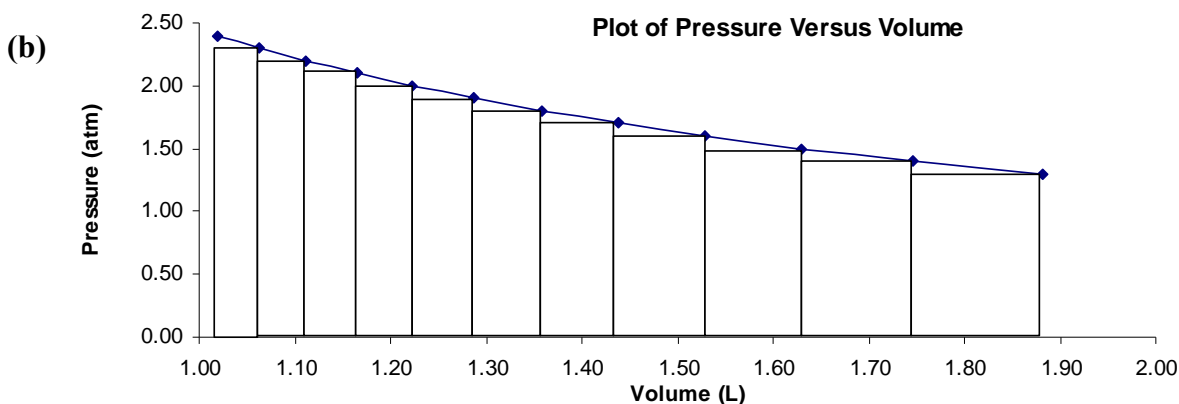For $P = 1.50$ atm: $V = 1.63$ L $P\Delta V = 1.50$ atm $\times -0.10$ L $= -0.15$ L atm
For $P = 1.40$ atm: $V = 1.75$ L $P\Delta V = 1.40$ atm $\times -0.12$ L $= -0.17$ L atm
For $P = 1.30$ atm: $V = 1.88$ L $P\Delta V = 1.30$ atm $\times -0.13$ L $= -0.17$ L atm

total work $= -\Sigma\ P\Delta V = -1.45$ L atm

Expressed in joules, the work is -1.45 L atm $\times 101.325$ J/L atm $= -147$ J.

(b)

Plot of Pressure Versus Volume

(graph with y-axis "Pressure (atm)" from 0.00 to 2.50, x-axis "Volume (L)" from 1.00 to 2.00)

(c) The total work done in the two-step expansion is minus one times the total of the area of the two rectangles under the graph, which turns out to be -1.29 L·atm or -131 J. In the 11-step expansion in (b), the total area of the rectangles is 1.45 L atm or -14$\underline{7}$ J. If the expansion were divided into a larger number of stages, the total area of the rectangles would be even greater. The maximum amount of work is for an expansion with an infinite number of stages and is equal to the area under the pressure-volume curve between $V = 1.02$ L and 1.88 L. This area is also obtained as the integral of the expression:

$dw = -PdV = -nRT(dV/V)$. The value obtained is:
$w = -nRT \times \ln V_f / Vi = 0.100$ mol $\times$ 8.3145 J mol^{-1} K^{-1} $\times$ 298 K $\times$ ln (1.88 L/1.02 L)
$w = -152$ J

(d) The maximum work of compression is for a one-stage compression using an external pressure of 2.40 atm and producing a compression in volume of 1.02 L $-$ 1.88 L =
-0.86 L: $w = -P\Delta V = (2.40$ atm $\times$ 0.86 L) $\times$ 101.33 J/L atm $= 209$ J

The minimum work would be that done in an infinite number of steps and would be the same as the work determined in (c) but with a positive sign, namely, +152 J.

(e) Because the internal energy of an ideal gas is a function only of temperature, and the temperature remains constant, $\Delta U = 0$. Because $\Delta U = q + w = 0$, q $= -w$. This means that -209 J corresponds to the maximum work of compression, and -152 J corresponds to the minimum work of compression.

(f) For the expansion described in part in (c),
$q = -w = nRT \ln V_f/Vi$ and $q/T = nR \ln V_f/V_i$
Because the terms on the right side are all constants or functions of state, so too is the term on the left, q/T. In Chapter 19, we learn that q/T is equal to ΔS, the change in a state function called *entropy*.

126. (D) We use the data in Table 7.1 to generate the plot, with the C_p of Ti added in to demonstrate how it fits in with the data. Below are the data table and the plot

Element	AW	1/Aw	Cp	AW*Cp
Mg	24.3	0.041152	1.024	24.8832
Al	26.98	0.037064	0.903	24.36294
P	30.97	0.032289	0.777	24.06369
S	32.06	0.031192	0.706	22.63436
Fe	55.85	0.017905	0.449	25.07665
Cu	63.55	0.015736	0.385	24.46675
As	74.92	0.013348	0.329	24.64868
Se	78.96	0.012665	0.321	25.34616
Te	127.6	0.007837	0.202	25.7752
Pb	207.19	0.004826	0.128	26.52032
Ti	47.88	0.020886	0.523	25.04124
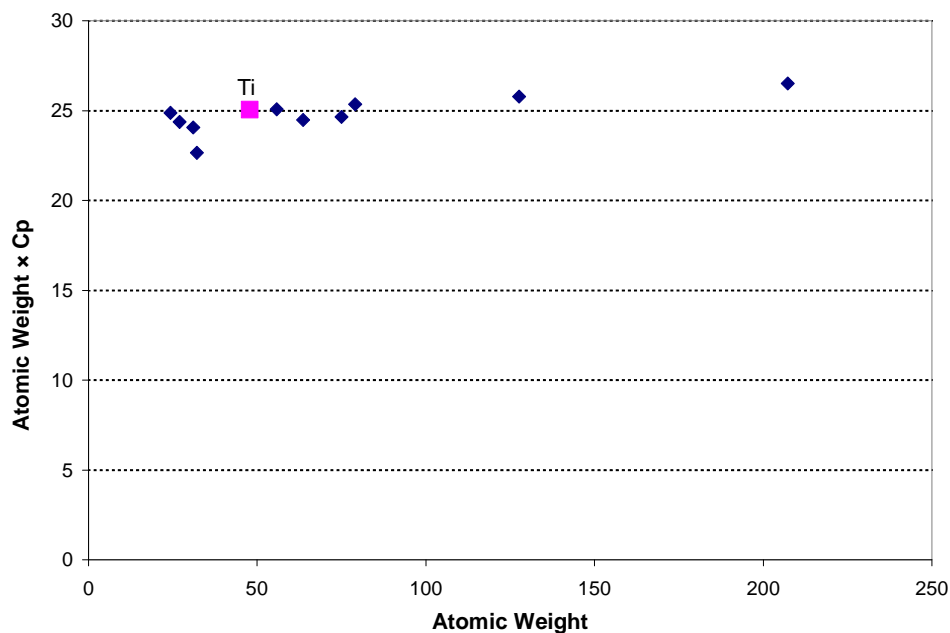
We can see that all the values in general center around 24 J/(mol·K) for all elements. This is known as the rule of Dulong-Petit. It is illustrated below in another way by plotting Cp versus the inverse of the atomic number. The slope of this line is ~24 J/(mol·K):
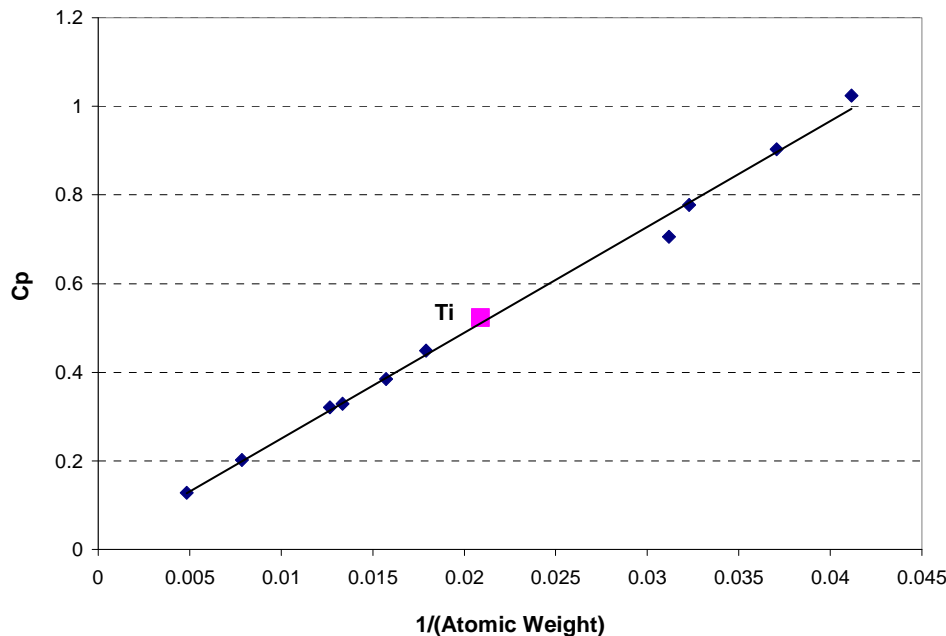
SELF-ASSESSMENT EXERCISES

127. (E)

    (a) ΔH: Enthalpy of the system, or the heat of the system at constant pressure

    (b) $P\Delta V$: Work done by the system (or on the system) through volume change at constant pressure

    (c) ΔH_f^0: Enthalpy of formation of a compound at standard conditions

    (d) Standard State: The pure element or compound under a pressure of 1 bar at a specified temperature

    (e) Fossil fuel: A fuel source generated by the decomposition of plant and animal matter in the crust of the earth

128. (E)

    (a) Law of conservation of energy: Energy is neither created nor destroyed (or stated differently, in the interaction between the system and the surroundings, the total energy of the system remains constant).

    (b) Bomb calorimetry: A method of determining heats of reaction (mainly combustion).

    (c) Function of state: A function that only depends on the state of the system, such as initial and final conditions, and is insensitive to how the state was established

    (d) Enthalpy diagram: A diagram that represents the enthalpy change in a system

    (e) Hess's Law: The enthalpy change of a process can be determined by summation of enthalpies of individual and elementary steps

129. (E)

    (a) System vs. surroundings: System is what we are studying. Surroundings is everything else.

(b) Heat vs. work: Heat is the flow of thermal energy. Work involves physical movement of an entity (whether microscopic or macroscopic)

(c) Specific heat vs. heat capacity: Heat capacity is the quantity of energy required to change the temperature of a substance by 1 degree. Specific heat is the heat capacity of 1 g of a substance.

(d) Constant volume vs. constant pressure process: A system where the reaction is done at a constant volume to eliminate work done by the system is a constant volume system. In a constant pressure system, there can be expansion and contraction and therefore work can be done.

130. **(E)** The answer is (b), Al, because it has the highest heat capacity.

131. **(E)** The answer is (c). We know that $m_1 c \Delta T_1 = - m_2 c \Delta T_2$, where m_1 and m_2 are the masses of each quantity of water. Therefore, the equation above can be expanded and simplified as follows:
$75 (T_f - 80) = -100 (T_f - 20)$
Solving for T_f gives a value of 45.7 °C.

132. **(E)** The answer is (d). $U = q + w$. Since $q = -100$ J, $w = +200$ J, or the system has 200 J of work done on it.

133. **(E)** The answer is (a). The heat generated by NaOH is absorbed by the system.

134. **(E)** The answer is (b). As graphite is burned in O_2, it generates CO_2. Enthalpy of formation of CO_2 is therefore the same as enthalpy of combustion of C.

135. **(E)** The answer is (a), because q_V and q_P are not the same.

136. **(E)**

(a) We have to solve for the heat capacity (C_p) of Fe:
$m \cdot C_p \cdot \Delta T (H_2O) = - m \cdot C_p \cdot \Delta T (Fe)$
$(981g)(4.189)(12.3 \,°C) = -(1220)(C_{P(Fe)})(-92.1 \,°C)$

Solving for Cp_{Fe}, the heat capacity of Fe is 0.449 $J \cdot g^{-1} \cdot °C^{-1}$

(b) Now knowing the Cp of Fe, we can calculate the T_f of the iron-glycerol system:

$(409.5)(2.378)(T_f - 26.2) = -(1220)(0.4489)(T_f - 99.8)$

Solving $T_f = 52.7$ °C

137. **(E)**
(a) $2 N_2 + O_2 \rightarrow 2 N_2O$
(b) $S + O_2 + Cl_2 \rightarrow SO_2Cl_2$
(c) $2 CH_3CH_2COOH + 7 O_2 \rightarrow 6 CO_2 + 6 H_2O$

138. **(D)** First, determine the ΔH_f^o of CO, which is used to make $COCl_2$. This is done by using the equations for the combustion of C and CO gases:

(1) $CO + ½ O_2 \rightarrow CO_2$ -283.0 kJ/mol
(2) $C + O_2 \rightarrow CO_2$ -393.5 kJ/mol

To determine the ΔH_f^o of CO, reverse and double equation (1) and double equation (2):

(1) $2 CO_2 \rightarrow 2 CO + O_2$	566.0 kJ
(2) $2C + 2 O_2 \rightarrow 2 CO_2$	-787.0 kJ
(3) $2 C + O_2 \rightarrow 2 CO$	-221.0 kJ
	or -110.5 kJ/mol of CO

Now, we use the equation for the formation of $COCl_2$ with equation (3) times ½.

(4) $CO + Cl_2 \rightarrow COCl_2$	-108.0 kJ
(3) $C + \frac{1}{2} O_2 \rightarrow CO$	-110.5 kJ
(3) $C + \frac{1}{2} O_2 + Cl_2 \rightarrow COCl_2$	-218.5 kJ

Therefore, ΔH_f^o of $COCl_2$ is -218 kJ/mol.

139. **(E)** Enthalpy of formation for elements (even molecular ones, such as O_2 or Cl_2) is by convention set to 0. While it is possible for the enthalpy of formation of a compound to be near zero, it is unlikely.

140. **(M)** We note that $\Delta H = \Delta U + \Delta(PV)$. From a theoretical standpoint, one can have a situation where the $\Delta U < 0$, but there is enough work done on the system that makes $\Delta H > 0$. In reality, because the $\Delta(PV)$ is relatively small, ΔH and ΔU often have the same sign.

141. **(M)** A gas stove works by combustion of a flammable fuel. The amount of heat can be controlled by a valve. Once shut off, the heat source instantly disappears. However, an electric stove works by the principle of heat conduction, where the heat coil on the stove transfers heat to the pot through direct contact. Even after the electricity is shut off to the heating coil, it takes time for the coil to cool because of its heat capacity, and therefore it continues to supply heat to the pot.

142. **(E)** The answer is (a), 0. This is because there is no loss of energy to or gain of energy from the surroundings.

143. **(M)** The answer is (b), the temperature decreases (or at least it increases at a slower rate than it would if there was no moisture on the outside). The moisture put outside of the pot evaporates mainly because of removing heat from the pot. Therefore, the moisture on the outside of the pot removes heat from the pot as it evaporates, therefore slightly cooling the pot.

144. **(M)** To construct a concept map, one must first start with the most general concepts. These concepts are not defined by or in terms of other concepts discussed in those sections. In this case, we are constructing a map for the first law of thermodynamics. After giving the definition, the concept can be broken up into two subtopics: functions of state, path-dependent functions. Functions of state should contain a discussion of ΔU. Path dependent functions should have a discussion of work (w) and heat (q). In the path dependent functions subsection, there should be a discussion on the nomenclature for determining heat and work flow in and out of the system.

Then, there should be a subheading for work, discussing the various forms of work (such as P-V work, for instance). A discussion of heat should contain subheadings for enthalpy at constant volume and pressure.

145. **(M)** The concept map of the use of enthalpy in chemical reactions has several major subheadings. After the definition of enthalpy, there should be three major subheadings: (1) expressing enthalpy graphically using enthalpy diagrams, (2) enthalpy of change for phase transformation, and (3) standard states and standard transformations. Then, under standard states and transformations, there would be further subheadings discussing (1) enthalpy of reaction, and (2) enthalpy of formation. Hess's law would be a subtopic for #1.

146. **(M)** This concept map starts with the root term, terms in thermodynamics. It is then split into the major subheadings, (1) path-dependent and (2) path-independent quantities. The remainder is very similar to question 144.