Answers to Exercise 6.1 Enthalpy and Hess' Law

1.

(a) The enthalpy change for a reaction is equal to the heat absorbed or released when that reaction is performed at constant pressure.

A reaction with a negative enthalpy change is exothermic (releases heat into the surroundings). Reactions with larger negative enthalpy changes release more heat.

A reaction with a positive enthalpy change is endothermic (absorbs heat from the surroundings). Reactions with larger positive enthalpy changes absorb more heat.

(b) Since the enthalpy change for a reaction is equal to the heat absorbed or released <u>at constant</u> <u>pressure</u>, it ought to be meaningful to discuss enthalpy changes for reactions performed at constant pressure. A common example would be reactions performed in open flasks (which are constantly at atmospheric pressure).

2.

$$Na_2CO_{3(s)} + 2H^+_{(aq)} \rightarrow 2Na^+_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$

Step 1: Check that chemical equation is balanced *It is.*

Step 2: Calculate standard enthalpy change for the reaction from the standard enthalpies of formation

$$\begin{split} \Delta_{r}H^{\circ} &= \sum \Delta_{f}H^{\circ}(products) - \sum \Delta_{f}H^{\circ}(reactants) \\ \Delta_{r}H^{\circ} &= \begin{bmatrix} 2 \ \Delta_{f}H^{\circ}(Na_{(aq)}^{+}) + \Delta_{f}H^{\circ}(H_{2}O_{(l)}) + \Delta_{f}H^{\circ}(CO_{2(g)}) \end{bmatrix} - \\ & \left[\Delta_{f}H^{\circ}(Na_{2}CO_{3(s)}) + 2 \ \Delta_{f}H^{\circ}(H_{(aq)}^{+}) \end{bmatrix} \\ \Delta_{r}H^{\circ} &= \begin{bmatrix} 2 \left(-240.1 \frac{kJ}{mol} \right) + \left(-285.8 \frac{kJ}{mol} \right) + \left(-393.5 \frac{kJ}{mol} \right) \end{bmatrix} - \left[\left(-1130.7 \frac{kJ}{mol} \right) + 2 \left(0 \frac{kJ}{mol} \right) \right] \\ \Delta_{r}H^{\circ} &= -28.8 \frac{kJ}{mol} \end{split}$$

Step 3: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

The calculated enthalpy change was negative, so this reaction should be exothermic.

Not counting $\Delta_f H^{\circ}(H^+_{(aq)})$ – which is defined as exactly $0 \frac{kJ}{mol}$ – the fewest number of decimal places for any value used in this calculation is one. Therefore, since the numbers are added/subtracted, the answer should have one decimal place.

3.

(a)
$$2 C_8 H_{18(l)} + 25 O_{2(g)} \rightarrow 16 CO_{2(g)} + 18 H_2 O_{(l)}$$

- (b) **Step 1: Write a balanced chemical equation for the reaction** *see part (a)*
 - Step 2: Calculate standard enthalpy change for the reaction from the standard enthalpies of formation

$$\begin{split} \Delta_{r}H^{\circ} &= \sum \Delta_{f}H^{\circ}(products) - \sum \Delta_{f}H^{\circ}(reactants) \\ \Delta_{r}H^{\circ} &= \begin{bmatrix} 16 \ \Delta_{f}H^{\circ}(CO_{2(g)}) + 18 \ \Delta_{f}H^{\circ}(H_{2}O_{(l)}) \end{bmatrix} - \begin{bmatrix} 2 \ \Delta_{f}H^{\circ}(C_{8}H_{18(l)}) + \\ 25 \ \Delta_{f}H^{\circ}(O_{2(g)}) \end{bmatrix} \\ &- 5470 \ \frac{kJ}{mol} = \begin{bmatrix} 16 \ \left(-393.5 \ \frac{kJ}{mol} \right) + 18 \ \left(-285.8 \ \frac{kJ}{mol} \right) \end{bmatrix} - \begin{bmatrix} 2 \ \Delta_{f}H^{\circ}(C_{8}H_{18(l)}) + 25 \ \left(0 \ \frac{kJ}{mol} \right) \end{bmatrix} \\ &- 5470 \ \frac{kJ}{mol} = -11440.4 \ \frac{kJ}{mol} - 2 \ \Delta_{f}H^{\circ}(C_{8}H_{18(l)}) \\ &5970 \ \frac{kJ}{mol} = -2 \ \Delta_{f}H^{\circ}(C_{8}H_{18(l)}) \\ &\Delta_{f}H^{\circ}(C_{8}H_{18(l)}) = -2985 \ \frac{kJ}{mol} \end{split}$$

Step 3: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

The calculated standard enthalpy of formation was negative. I checked my work by plugging my standard enthalpy of formation back into the initial $\Delta_r H^\circ = \dots$ equation to check that it gave the correct standard enthalpy change for the reaction.

4. Step 1: Generate a Set of Balanced Equations that Can Be Combined to Give the Required Overall Equation

$2 \operatorname{Na}_{(s)} + H_{2(g)} \to 2 \operatorname{NaH}_{(s)}$	$\Delta H^{\circ} = 2 \Delta H_f^{o} \left(NaH_{(s)} \right) = -112.56 \frac{kJ}{mol}$
$2 \operatorname{Na}_{(l)} \to 2 \operatorname{Na}_{(s)}$	$\Delta H^{\circ} = -2\left(2.6\frac{kJ}{mol}\right) = -5.2\frac{kJ}{mol}$
$2 \operatorname{Na}_{(l)} + H_{2(g)} \to 2 \operatorname{Na}_{(s)}$	

Standard enthalpy of formation is the enthalpy change for the formation of a compound from its constituent elements in the standard state. The standard enthalpy of formation for $NaH_{(s)}$ is for the reaction producing 1 mol $NaH_{(s)}$. Since enthalpy is an extrinsic property, the enthalpy change for formation of 2 mol $NaH_{(s)}$ will be twice as much.

In order to get the equations to add up to the desired overall equation, the melting of sodium equation must be reversed to show liquid sodium be frozen to solid sodium. When the equation is flipped, the sign of the enthalpy change is reversed. Since we both flip the equation and multiply it by two, we must multiply the provided enthalpy change by -2.

Step 2: Use Hess' Law to Calculate the Standard Enthalpy Change

Hess' Law states that the enthalpy change for any reaction is equal to the sum of the enthalpy changes for reactions that add up to that overall reaction. As such, if we add the standard enthalpy changes for the two steps, we get the standard enthalpy change for the overall reaction.

$$\Delta_r H^\circ = \left(-112.56 \frac{kJ}{mol}\right) + \left(-5.2 \frac{kJ}{mol}\right)$$
$$\Delta_r H^\circ = -117.8 \frac{kJ}{mol}$$

Step 3: Check your work

Does your answer seem reasonable? Are sig. fig. correct?