Most Important Ideas:
1. \( \Delta H_f^0 = \sum n \Delta H_f^0(\text{products}) - \sum m \Delta H_f^0(\text{reactants}) \)

2. Example: for the equation \( aA + bB \rightarrow cC + dD \):
\[
\Delta H_{rxn}^0 = [c \Delta H_f^0(C) + d \Delta H_f^0(D)] - [a \Delta H_f^0(A) + b \Delta H_f^0(B)]
\]

**Objective**
The purpose of this activity is to calculate the \( \Delta H_f^0 \) of a substance using the direct method. This method is used when the \( \Delta H_f^0 \) values are known for the compounds involved in the reaction.

**Reference**

**Background**
The standard enthalpy of formation (\( \Delta H_f^0 \)) for a substance is the ‘sea level’ reference for determining its enthalpy, and indicates the relative stability of a substance. The superscript “0” represents the standard-state conditions. Not to be confused with STP (0°C and 1 atm), standard-state conditions are 1 atm and 25°C.

Because we can only know the relative enthalpy of a substance (not its absolute enthalpy), chemists have assigned \( \Delta H_f^0 = 0 \) for elements in their most stable forms at standard-state conditions against all other substances are measured. For example, hydrogen exists as \( \text{H}_2 \) at standard-state conditions so \( \Delta H_f^0(\text{H}_2, \text{gas}) = 0 \text{kJ/mol} \) and \( \Delta H_f^0(\text{H}, \text{gas}) \neq 0 \text{kJ/mol} \).

There are two methods used to determine the standard heat of formation (\( \Delta H_f^0 \)) of a substance:

1. Direct Method: \( \Delta H_f^0 \) values are known for the compounds involved, and
2. Indirect Method (a.k.a., Hess’s law): the overall reaction is broken down in to a series of steps with known enthalpies.

The direct method uses the difference between \( \Delta H_f^0 \) of the products and \( \Delta H_f^0 \) of the reactants:
\[
\Delta H_{rxn}^0 = [\text{sum of enthalpies of formation of products}] - [\text{sum of enthalpies of formation of reactants}]
\]

In equation form:
\[
\Delta H_{rxn}^0 = \sum n \Delta H_f^0(\text{products}) - \sum m \Delta H_f^0(\text{reactants})
\]

Where:
- \( \Sigma = \text{sum} \)
- \( n \& m = \text{the stoichiometric coefficients for the products \& reactants, respectively.} \)

\[1 \Delta H_f^0(\text{H, gas}) = 218.2 \text{kJ/mol} \]
N.B. State symbols are very important for these calculations. (E.g., $\Delta H_f^0$ for liquid water is different from that of $\Delta H_f^0$ for gas (steam) or $\Delta H_f^0$ for solid (ice).

**Model**

**Problem**

Calculate the $\Delta H_f^0$ for glucose from the combustion reaction:

$$\text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \quad \Delta H_{rxn}^0 = -2821.8 \text{ kJ/mol}$$

Given: $\Delta H_f^0(\text{CO}_2, g) = -393.5 \text{ kJ/mol}$, and $\Delta H_f^0(\text{H}_2\text{O}, l) = -285.8 \text{ kJ/mol}$.

Why is $\Delta H_f^0(\text{O}_2, g) = 0 \text{ kJ/mol}$?

**Solution**

$$\Delta H_{rxn}^0 = [(6 \times \Delta H_f^0(\text{CO}_2, g)) + (6 \times \Delta H_f^0(\text{H}_2\text{O}, l))]$$

$$= [(6 \times -393.5 \text{ kJ/mol}) + (6 \times -285.8 \text{ kJ/mol})]$$

$$= [(-2361.0) + (-1714.8)] - [\Delta H_f^0(\text{C}_6\text{H}_{12}\text{O}_6, s)]$$

$$\Delta H_f^0(\text{C}_6\text{H}_{12}\text{O}_6, s) = (-4075.8 + 2821.5) \text{ kJ/mol}$$

$$\Delta H_f^0(\text{C}_6\text{H}_{12}\text{O}_6, s) = -1250.3 \text{ kJ/mol}$$
Problems

1. Which of the following standard enthalpy of formation values is not zero at 25°C? Na(s), Ne(g), CH₄(g), S₈(s), Hg(l), H(g).

   ANS
   CH₄(g) and H(g). All the other choices are elements in their most stable form (ΔHᵋ = 0). The most stable form of hydrogen is H₂(g).

2. The ΔHᵋ values of the two allotropes of oxygen, O₂ and O₃, are 0 and 142.2 kJ/mol, respectively, at 25°C. Which is the more stable form at this temperature?

   ANS
   The standard enthalpy of formation of any element in its most stable form is zero. Therefore, since ΔHᵋ(O₂) = 0, O₂ is the more stable form of the element oxygen at this temperature.

3. Which is the more negative quantity at 25°C: ΔHᵋ for H₂O(l) or ΔHᵋ for H₂O(g)?

   ANS
   H₂O(l) → H₂O(g) Endothermic
   ΔHᵋ = ΔHᵋ[H₂O(g)] - ΔHᵋ[H₂O(l)] > 0
   ΔHᵋ[H₂O(l)] is more negative since ΔHᵋ > 0.
   You could also solve the problem by realizing that H₂O(l) is the stable form of water at 25°C, and therefore will have the more negative ΔHᵋ value.

4. Predict the value of ΔHᵋ (greater than, less than, or equal to zero) for these elements at 25°C: (a) Br₂(g) and Br₂(l), (b) I₂(g) and I₂(s).

   ANS
   (a) Br₂(l) is the most stable form of bromine at 25°C; therefore, ΔHᵋ[Br₂(l)] = 0. Since Br₂(g) is less stable than Br₂(l), ΔHᵋ[Br₂(g)] > 0.
   (b) I₂(s) is the most stable form of iodine at 25°C; therefore, ΔHᵋ[I₂(s)] = 0. Since I₂(g) is less stable than I₂(s), ΔHᵋ[I₂(g)] > 0.
5. In general, compounds with negative values are more stable than those with positive $\Delta H_f^0$ values. $\text{H}_2\text{O}_2(\text{l})$ has a negative $\Delta H_f^0$ ($-187.6 \text{ kJ/mol}$). Why, then, does $\text{H}_2\text{O}_2(\text{l})$ have a tendency to decompose to $\text{H}_2\text{O}(\text{l})$ and $\text{O}_2(\text{g})$?

ANS

$$2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$$

$\text{H}_2\text{O}_2(\text{l})$ has a tendency to decompose because $\text{H}_2\text{O}(\text{l})$ has a more negative $\Delta H_f^0$ than $\text{H}_2\text{O}_2(\text{l})$.

6. Suggest ways (with appropriate equations) that would enable you to measure the $\Delta H_f^0$ values of $\text{Ag}_2\text{O}(\text{s})$ and $\text{CaCl}_2(\text{s})$ from their elements. No calculations are necessary.

ANS

Strategy: What is the reaction for the formation of $\text{Ag}_2\text{O}$ from its elements? What is the $\Delta H_f^0$ value for an element in its standard state?

Solution: The balanced equation showing the formation of $\text{Ag}_2\text{O}(\text{s})$ from its elements is:

$$2\text{Ag}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{Ag}_2\text{O}(\text{s})$$

Knowing that the standard enthalpy of formation of any element in its most stable form is zero, and using Equation (6.18) of the text, we write:

$$\Delta H_{\text{rxn}} = \sum n\Delta H_f^0 \text{(products)} - \sum m\Delta H_f^0 \text{(reactants)}$$

$$\Delta H_{\text{rxn}}^0 = [\Delta H_f^0(\text{Ag}_2\text{O})] - [2\Delta H_f^0(\text{Ag}) + \frac{1}{2}\Delta H_f^0(\text{O}_2)]$$

$$\Delta H_{\text{rxn}}^0 = [\Delta H_f^0(\text{Ag}_2\text{O})] - [0 + 0]$$

$$\Delta H_f^0(\text{Ag}_2\text{O}) = \Delta H_{\text{rxn}}^0$$

In a similar manner, you should be able to show that $\Delta H_f^0(\text{CaCl}_2) = \Delta H_{\text{rxn}}^0$ for the reaction

$$\text{Ca}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$$

7. Calculate the heat of decomposition for this process at constant pressure and $25^\circ\text{C}$:

$$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

$\Delta H_f^0(\text{CaCO}_3, \text{s}) = -1206.9 \text{ kJ/mol}$; $\Delta H_f^0(\text{CaO, s}) = -635.6 \text{ kJ/mol}$; $\Delta H_f^0(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$

ANS

$$\Delta H^0 = [\Delta H_f^0(\text{CaO}) + \Delta H_f^0(\text{CO}_2)] - \Delta H_f^0(\text{CaCO}_3)$$

$$\Delta H^0 = [(1)(-635.6 \text{ kJ/mol}) + (1)(-393.5 \text{ kJ/mol})] - (1)(-1206.9 \text{ kJ/mol}) = 177.8 \text{ kJ/mol}$$
8. The standard enthalpies of formation of ions in aqueous solutions are obtained by arbitrarily assigning a value of zero to H\(^+\) ions; that is, \(\Delta H_f^0([H^+(aq)]) = 0\).  

\[ \text{(6.52)} \]

a. For the following reaction: 
\[ \text{HCl}(s) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq) \] 
\( \Delta H_{rxn}^0 = -74.9 \text{ kJ/mol} \) 

calculate \( \Delta H_f^0 \) for the \( \text{Cl}^- \) ions.

\[ \text{ANS} \]

Strategy: The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants. The enthalpy of each species (reactant or product) is given by the product of the stoichiometric coefficient and the standard enthalpy of formation, \( \Delta H_f^\circ \), of the species.

Solution: We use the \( \Delta H_f^\circ \) values in Appendix 2 and Equation (6.18) of the text.

\[
\Delta H_{rxn}^\circ = \sum n\Delta H_f^\circ \text{(products)} - \sum m\Delta H_f^\circ \text{(reactants)}
\]

\[
\text{HCl}(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)
\]

\[
\Delta H_{rxn}^\circ = \Delta H_f^\circ \text{(H}^+) + \Delta H_f^\circ \text{(Cl}^-) - \Delta H_f^\circ \text{(HCl)}
\]

\[-74.9 \text{ kJ/mol} = 0 + \Delta H_f^\circ \text{(Cl}^-) - (1)(-92.3 \text{ kJ/mol})
\]

\[
\Delta H_f^\circ \text{(Cl}^-) = -167.2 \text{ kJ/mol}
\]

b. Given that \( \Delta H_f^0 \) for \( \text{OH}^- \) ions is \(-229.6 \text{ kJ/mol}\), calculate the enthalpy of neutralization when 1 mole of a strong monoprotic acid (such as HCl) is titrated by 1 mole of a strong base (such as KOH) at 25\(^\circ\)C.

\[ \text{ANS} \]

The neutralization reaction is:

\[
\text{H}^+(aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l)
\]

and,

\[
\Delta H_{rxn}^\circ = \Delta H_f^\circ \text{[H}_2\text{O}(l)] - [\Delta H_f^\circ \text{(H}^+) + \Delta H_f^\circ \text{(OH}^-)]]
\]

\[
\Delta H_f^\circ \text{[H}_2\text{O}(l)] = -285.8 \text{ kJ/mol} \text{ (See Appendix 2 of the text.)}
\]

\[
\Delta H_{rxn}^\circ = (1)(-285.8 \text{ kJ/mol}) - [(1)(0 \text{ kJ/mol}) + (1)(-229.6 \text{ kJ/mol})] = -56.2 \text{ kJ/mol}
\]