Thermochemistry 4: Standard Enthalpies of Formation

Learning Objective	Openstax 2e Chapter
Standard Enthalpies of Formation	5.3

Suggested Practice Problems

Chapter 5 Exercises – Questions: 55*, 69, 71, 83

Answers can be found in the Chapter 5 Answer Key

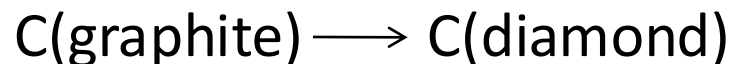*Use Appendix G for the standard enthalpies of formation

Standard Enthalpies of Formation

- The **standard state** is the state of a material at a defined set of conditions
    - pure gas at exactly 100 kPa pressure
    - pure solid or liquid at exactly 100 kPa pressure and temperature of interest
        - usually 25°C
    - substance in a solution with a concentration of 1 M

- The **standard enthalpy of formation, $\Delta_f H°$,** is the enthalpy change for the reaction forming <u>1 mole of a pure compound</u> from its <u>constituent elements</u>
    - The elements must be in their standard states
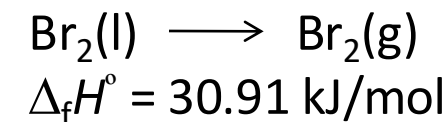   - By definition, the $\Delta_f H°$ for a pure element in its reference form and standard state is 0 kJ/mol

Reference Form of a Pure Element

- Typically, the most stable form of the element under standard conditions:
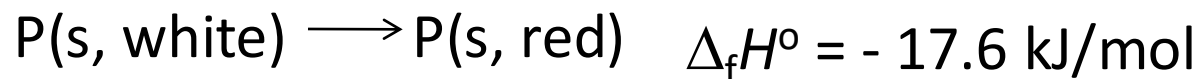
    $Na(s)$, $H_2(g)$, $O_2(g)$, $Br_2(l)$, C(graphite)

$$C(graphite) \longrightarrow C(diamond)$$

$$\Delta_f H^o = 1.9 \text{ kJ/mol}$$

$$Br_2(l) \longrightarrow Br_2(g)$$
$$\Delta_f H^\circ = 30.91 \text{ kJ/mol}$$

- Phosphorus element is an exception:

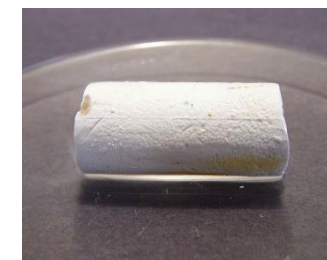 $$P(s, white) \longrightarrow P(s, red) \quad \Delta_f H^o = -17.6 \text{ kJ/mol}$$

The less stable white phosphorus is defined as the reference form! (easier to prepare in high purity)

Red Phosphorous

White Phosphorous

$\Delta_f H^\circ = -17.6 \text{ kJ/mol}$ $\Delta_f H^\circ = 0$

Writing Formation Reactions

Write the formation reaction for CO(g)

- The formation reaction is the reaction involving the elements in the compound, which are C and O:

- The elements must be in their **standard state** (298.15 K, 100 kPa)
  - there are several forms of solid C, but the one with $\Delta_f H^o$ defined as 0 kJ/mol is graphite
  - oxygen's standard state is the diatomic gas, O$_2$(gas)

- The equation must be balanced, but the coefficient of the product compound must be 1
  - use coefficients in front of the reactants (including fractions if necessary) to make the atoms on both sides equal without changing the product coefficient

$$C + O \rightarrow CO(g)$$

$$C(s, graphite) + O_2(g) \rightarrow CO(g)$$

$$C(s, graphite) + \tfrac{1}{2}\, O_2(g) \rightarrow CO(g)$$
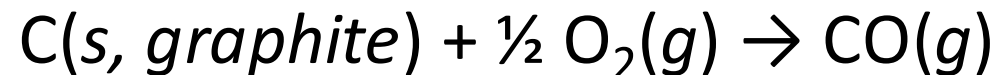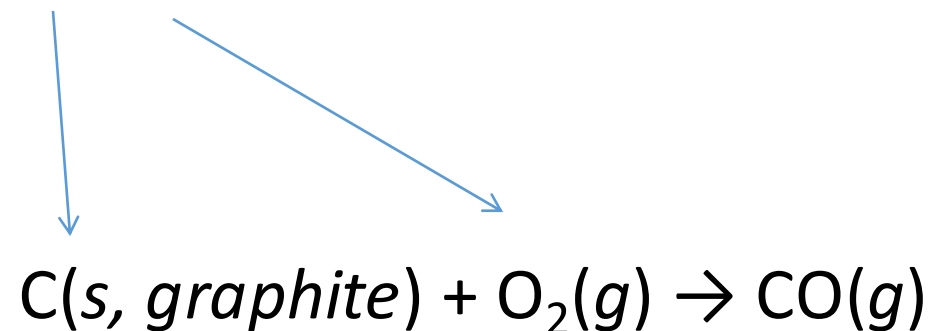
Standard Enthalpies of Formation: $\Delta_f H°$

The reaction enthalpy for the standard formation reaction is the standard enthalpy of formation, $\Delta_f H°$.

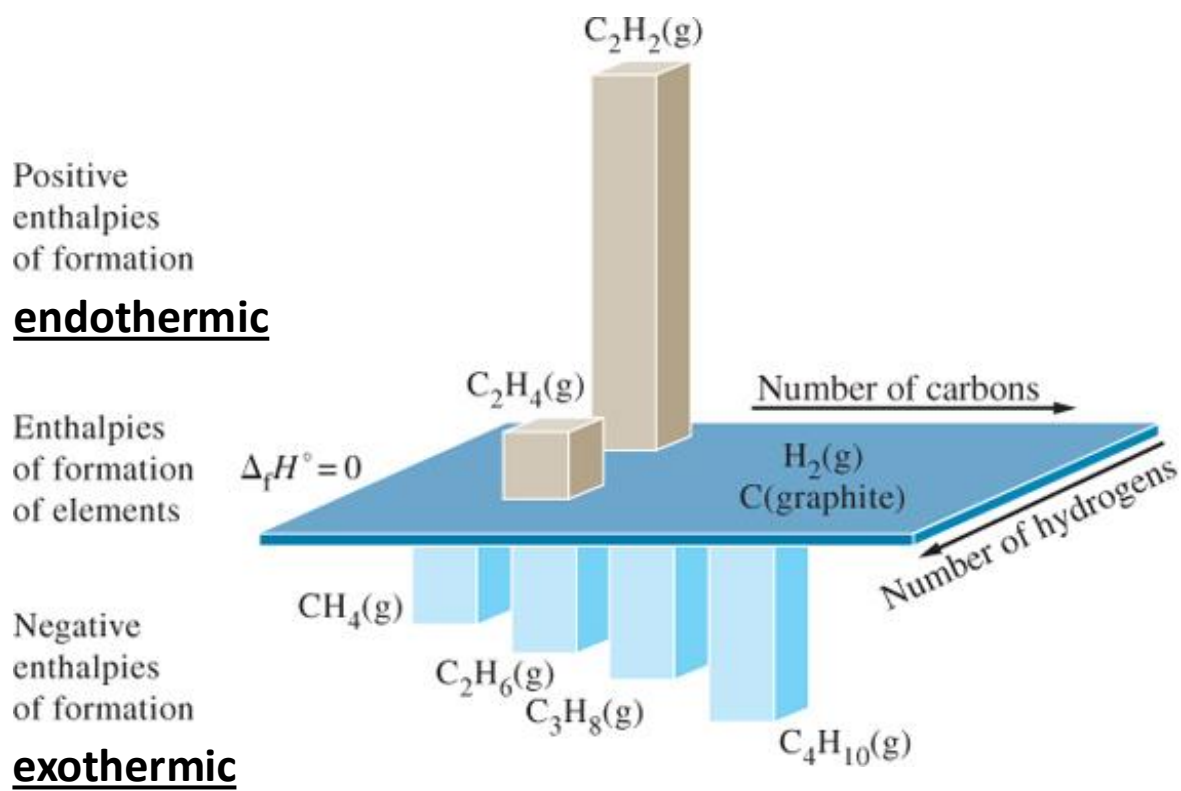**Figure 1:** Enthalpy of formation for hydrocarbons

TABLE 7.2 Some Standard Molar Enthalpies of Formation, $\Delta_f H°$ at 298.15 K			
Substance	kJ/mol[a]	Substance	kJ/mol[a]
$CO(g)$	−110.5	$HBr(g)$	−36.40
$CO_2(g)$	−393.5	$HI(g)$	26.48
$CH_4(g)$	−74.81	$H_2O(g)$	−241.8
$C_2H_2(g)$	226.7	$H_2O(l)$	−285.8
$C_2H_4(g)$	52.26	$H_2S(g)$	−20.63
$C_2H_6(g)$	−84.68	$NH_3(g)$	−46.11
$C_3H_8(g)$	−103.8	$NO(g)$	90.25
$C_4H_{10}(g)$	−125.6	$N_2O(g)$	82.05
$CH_3OH(l)$	−238.7	$NO_2(g)$	33.18
$C_2H_5OH(l)$	−277.7	$N_2O_4(g)$	9.16
$HF(g)$	−271.1	$SO_2(g)$	−296.8
$HCl(g)$	−92.31	$SO_3(g)$	−395.7

[a]Values are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.

Enthalpy of formation is related to molecular structure.

What are common for those hydrocarbons with positive and negative enthalpies?

Calculation of Standard Enthalpies of Reaction $\Delta_r H°$ from $\Delta_f H°$

$$\text{Reactants} \longrightarrow \text{Products}$$

$$\Delta_r H° = \sum_{i \in Products} n_i \times \Delta_f H°(i^{th}\ product) - \sum_{j \in Reactants} n_j \times \Delta_f H°(j^{th}\ reactant)$$

where,

- n_i and n_j are stoichiometric coefficients in the reaction equation.
- units of $\Delta_r H°$ and $\Delta_f H°$ are kJ/mol.

Meaning of **kJ/mol** for the reaction refers to enthalpy change *per mole of reaction* (as written).

Example 1: Determine the standard enthalpy of reaction for the following reaction.

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g) \qquad \Delta_r H^\circ = ?$$
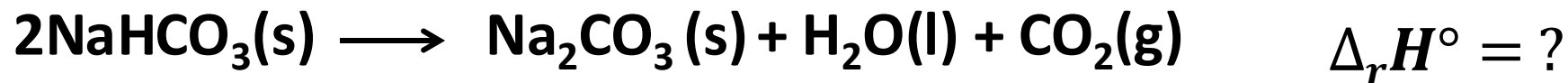
Reactant(s)   Product(s)

Solution: $\Delta_r H^\circ = [\Delta_f H^\circ_{Na_2CO_3} + \Delta_f H^\circ_{H2O} + \Delta_f H^\circ_{CO2}] - [2\,\Delta_f H^\circ_{NaHCO_3}]$

Product(s)   Reactant(s)

Another equivalent approach is to decompose reactant(s) into reference state, followed by recombination of them into products. Then use Hess's Law.
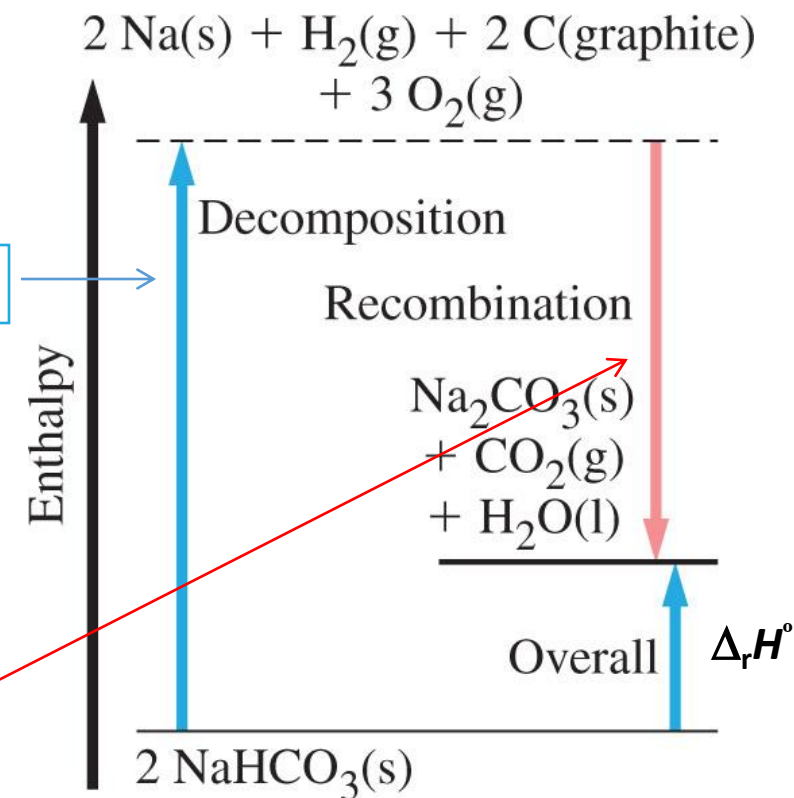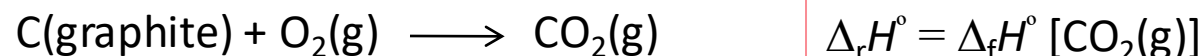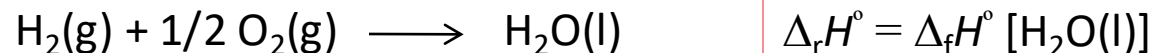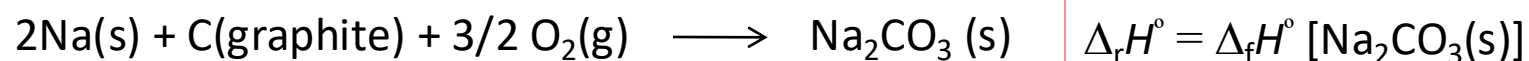
2NaHCO$_3$(s) $\longrightarrow$ **Na$_2$CO$_3$(s) + H$_2$O(l) + CO$_2$(g)** $\quad \Delta_r H^{\circ}$ = ?
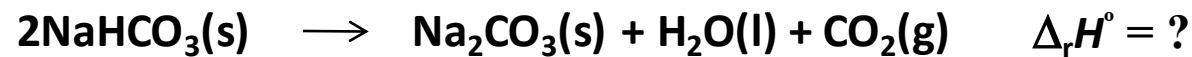
Reactant(s) $\qquad$ Product(s)

Decomposition of reactant(s)

2NaHCO$_3$(s) $\longrightarrow$ 2Na(s) + H$_2$(g) + 2C (graphite) + 3O$_2$(g) $\boxed{\Delta_r H^{\circ} = \mathbf{-2} \times \Delta_f H^{\circ} [\text{NaHCO}_3(s)]}$

Recombination of products

2Na(s) + C(graphite) + 3/2 O$_2$(g) $\longrightarrow$ Na$_2$CO$_3$ (s) $\quad \boxed{\Delta_r H^{\circ} = \Delta_f H^{\circ} [\text{Na}_2\text{CO}_3(s)]}$

H$_2$(g) + 1/2 O$_2$(g) $\longrightarrow$ H$_2$O(l) $\quad \boxed{\Delta_r H^{\circ} = \Delta_f H^{\circ} [\text{H}_2\text{O}(l)]}$

C(graphite) + O$_2$(g) $\longrightarrow$ CO$_2$(g) $\quad \boxed{\Delta_r H^{\circ} = \Delta_f H^{\circ} [\text{CO}_2(g)]}$

$2 \text{Na(s)} + \text{H}_2\text{(g)} + 2\,\text{C(graphite)} + 3\,\text{O}_2\text{(g)}$

Enthalpy

Decomposition

Recombination

$\text{Na}_2\text{CO}_3\text{(s)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$

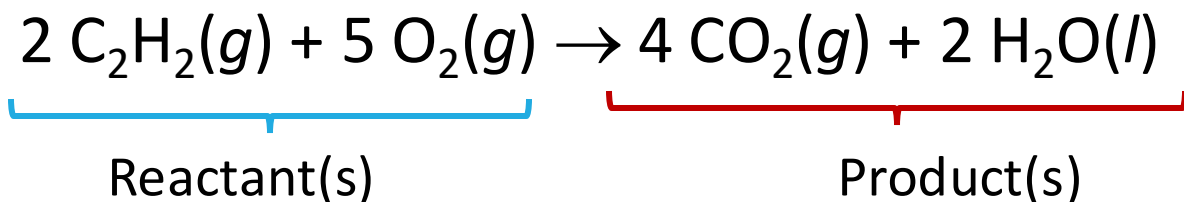Overall $\quad \Delta_r H^{\circ}$

$2\,\text{NaHCO}_3\text{(s)}$

$$\Delta_r H^{\circ} = [\Delta_f H^{\circ}{}_{\text{Na}_2\text{CO}_3} + \Delta_f H^{\circ}{}_{\text{H2O}} + \Delta_f H^{\circ}{}_{\text{CO2}}] - [2\,\Delta_f H^{\circ}{}_{\text{NaHCO}_3}]$$

Product(s) $\qquad\qquad$ Reactant(s)

Example 2: Determine the standard enthalpy of reaction for the following reaction.

$$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$$

Reactant(s)   Product(s)

TABLE 7.2 Some Standard Molar Enthalpies of Formation, $\Delta_f H°$ at 298.15 K

Substance	kJ/mol[a]	Substance	kJ/mol[a]
$CO(g)$	−110.5	$HBr(g)$	−36.40
$CO_2(g)$	−393.5	$HI(g)$	26.48
$CH_4(g)$	−74.81	$H_2O(g)$	−241.8
$C_2H_2(g)$	226.7	$H_2O(l)$	−285.8
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$HF(g)$	−271.1	$SO_2(g)$	−296.8
$HCl(g)$	−92.31	$SO_3(g)$	−395.7

[a]Values are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.

Solution:

$$\Delta_r H° = [4\ \Delta_f H°(CO_2) + 2\ \Delta_f H°(H_2O)] - [2\ \Delta_f H°(C_2H_2) + 5\ \Delta_f H°(O_2)]$$
$$= [4 \times (-393.5) + 2 \times (-285.8)] - [2 \times 226.7 + 5 \times 0]$$
$$= -2599.0\ \text{kJ/mol}$$

Alternatively, using Hess's Law:

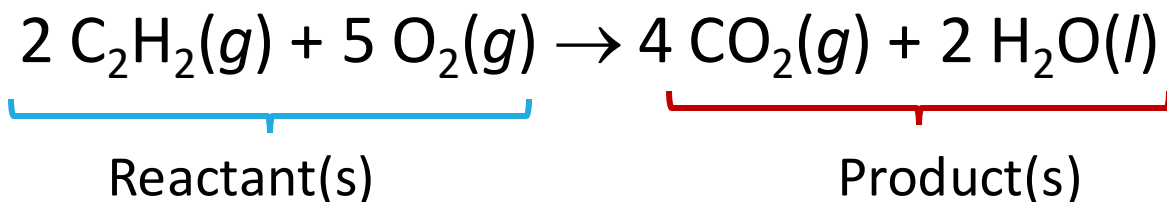$$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$$

Reactant(s)   Product(s)

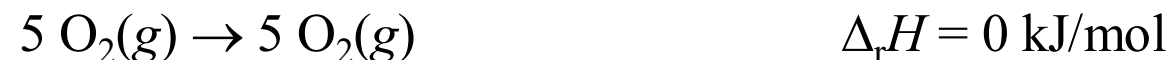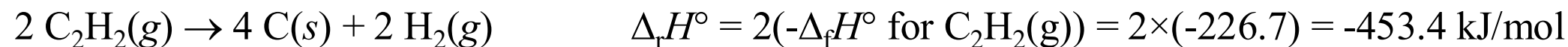**TABLE 7.2** Some Standard Molar Enthalpies of Formation, $\Delta_f H°$ at 298.15 K

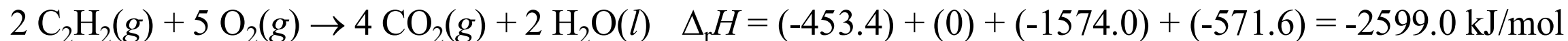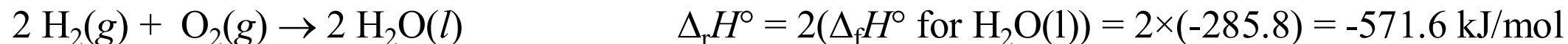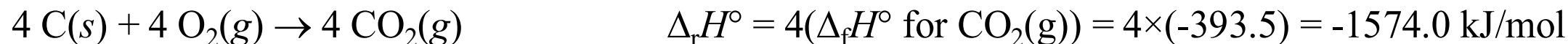| Substance	kJ/mol[a]	Substance	kJ/mol[a]
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$HCl(g)$	−92.31	$SO_3(g)$	−395.7

[a]Values are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.

1. Decompose each reactant into its reference state

$2\ C_2H_2(g) \rightarrow 4\ C(s) + 2\ H_2(g)$ $\Delta_r H° = 2(-\Delta_f H°\ \text{for}\ C_2H_2(g)) = 2\times(-226.7) = -453.4\ \text{kJ/mol}$

$5\ O_2(g) \rightarrow 5\ O_2(g)$ $\Delta_r H = 0\ \text{kJ/mol}$

2. Recombine the products from the above decomposition reactions into real products

$4\ C(s) + 4\ O_2(g) \rightarrow 4\ CO_2(g)$ $\Delta_r H° = 4(\Delta_f H°\ \text{for}\ CO_2(g)) = 4\times(-393.5) = -1574.0\ \text{kJ/mol}$

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ $\Delta_r H° = 2(\Delta_f H°\ \text{for}\ H_2O(l)) = 2\times(-285.8) = -571.6\ \text{kJ/mol}$

$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$ $\Delta_r H = (-453.4) + (0) + (-1574.0) + (-571.6) = -2599.0\ \text{kJ/mol}$

How to determine $\Delta_f H^o$ for reactions involving ions in solution?

Many chemical reactions in aqueous solution are best thought of as reactions between ions and best represented by net ionic equations. For example,

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta_r H^0 = -55.8 \frac{kJ}{mol}$$
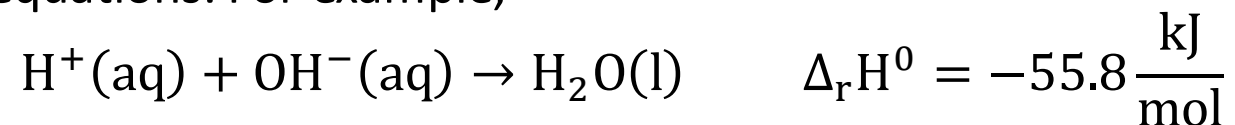
Enthalpies of formation in solution depend upon solute concentration. These data are representative for aqueous solutions at standard state (1 M). $\Delta_f H°$ [1 M H$^+$(aq)] = 0, by definition.

We can write $\Delta_r H°$ in terms of $\Delta_f H°$, and determine the enthalpy of formation for OH$^-$(aq)

$$\Delta_r H^0 = 1 \times \Delta_f H^0[H_2O(l)] - \{1 \times \Delta_f H^0[H^+(aq)] + 1 \times \Delta_f H^0[OH^-(aq)]\} = -55.8 \frac{kJ}{mol}$$

Then we have

$$\Delta_f H^0[OH^-(aq)]$$
$$= 55.8 \frac{kJ}{mol} + 1 \times \Delta_f H^0[H_2O(l)] - 1 \times \Delta_f H^0[H^+(aq)]$$
$$\Delta_f H^0[OH^-(aq)] = 55.8 \frac{kJ}{mol} - 285.8 \frac{kJ}{mol} - 0 \frac{kJ}{mol}$$
$$\mathbf{\Delta_f H^0[OH^-(aq)] = -230.0 \frac{kJ}{mol}}$$

TABLE 7.3 Some Standard Molar Enthalpies of Formation, $\Delta_f H°$ of Ions in Aqueous Solution at 298.15 K

Ion	kJ/mol	Ion	kJ/mol
H$^+$	0	OH$^-$	−230.0
Li$^+$	−278.5	Cl$^-$	−167.2
Na$^+$	−240.1	Br$^-$	−121.6
K$^+$	−252.4	I$^-$	−55.19
NH$_4^+$	−132.5	NO$_3^-$	−205.0
Ag$^+$	105.6	CO$_3^{2-}$	−677.1
Mg^{2+}	−466.9	S^{2-}	33.05
Ca^{2+}	−542.8	SO$_4^{2-}$	−909.3
Ba^{2+}	−537.6	S$_2$O$_3^{2-}$	−648.5
Cu^{2+}	64.77	PO$_4^{3-}$	−1277
Al^{3+}	−531		