Learning Objectives

- To know the key features of a state function.
- To use Hess’s law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Both heat and work represent energy transfer mechanisms. As discussed previously, the term "heat" refers to a process in which a body (the contents of a tea kettle, for example) acquires or loses energy as a direct consequence of its having a different temperature than its surroundings. Similarly, work refers to the transfer of energy that does not involve temperature differences. Hence, work, like energy, can take various forms, the most familiar being mechanical and electrical.

- **Mechanical work** arises when an object moves a distance \(\Delta x\) against an opposing force \(f\): \[ w_{\text{mechanical}} = f \Delta x \]
- **Electrical work** is done when a body having a charge \(q\) moves through a potential difference \(\Delta V\). \[ w_{\text{electrical}} = q \Delta V \]

The unit of work is Joules. Work, like heat, exists only when energy is being transferred. When two bodies are placed in thermal contact and energy flows from the warmer body to the cooler one, this process is called “heat”. A transfer of energy to or from a system by any means other than heat is called “work”.

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**Enthalpy as a Composite Function**

To further understand the relationship between heat flow (q) and the resulting change in internal energy (\(\Delta U\)), we can look at two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure. We will assume that PV work is the only kind of work possible for the system, so we can substitute its definition from Equation \(\text{ref}(18.5)\) into Equation \(\text{ref}(5.2.5)\) to obtain the following:

\[
\Delta U = q - P \Delta V \quad \text{label}(5.2.5)
\]

where the subscripts have been deleted.

If the reaction occurs in a closed vessel, the volume of the system is fixed, and \(\Delta V\) is zero. Under these conditions, the heat flow (often given the symbol \(q_v\) to indicate constant volume) must equal \(\Delta U\):

\[
\underset{\text{constant volume}}{q_v = \Delta U} \quad \text{label}(5.3.3)
\]

At constant volume, no \(PV\) work can be done, and the change in the internal energy of the system is equal to the amount of heat transferred from the system to the surroundings or vice versa.

Many chemical reactions are not, however, carried out in sealed containers at constant volume but in open containers at a more or less constant pressure of about 1 atm. The heat flow under these conditions is given the symbol \(q_p\) to indicate constant pressure. Replacing \(q\) in Equation \(\text{ref}(5.3.3)\) by \(q_p\) and rearranging to solve for \(q_p\),

\[
\underset{\text{constant pressure}}{q_p = \Delta U + P \Delta V} \quad \text{label}(5.3.4)
\]

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the PV work done.
Because conditions of constant pressure are so important in chemistry, a new state function called enthalpy (H) is defined as

\[ H = U + PV \]

At constant pressure, the change in the enthalpy of a system is as follows:

\[ \Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V \tag{5.3.5} \]

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: \( \Delta H = q_p \). This expression is consistent with our definition of enthalpy, where we stated that enthalpy is the heat absorbed or produced during any process that occurs at constant pressure.

Example \( \PageIndex{1} \)

The molar enthalpy of fusion for ice at 0.0°C and a pressure of 1.00 atm is 6.01 kJ, and the molar volumes of ice and water at 0°C are 0.0197 L and 0.0180 L, respectively. Calculate \( \Delta H \) and \( \Delta U \) for the melting of ice at 0.0°C.

**Given:** enthalpy of fusion for ice, pressure, and molar volumes of ice and water

**Asked for:** \( \Delta H \) and \( \Delta U \) for ice melting at 0.0°C

**Strategy:**

A. Determine the sign of \( q \) and set this value equal to \( \Delta H \).

B. Calculate \( \Delta(PV) \) from the information given.

C. Determine \( \Delta U \) by substituting the calculated values into Equation \( \ref{5.3.5} \).

**SOLUTION**

A. Because 6.01 kJ of heat is absorbed from the surroundings when 1 mol of ice melts, \( q = +6.01 \) kJ. When the process is carried out at constant pressure, \( q_p = \Delta H = 6.01 \) kJ.

B. To find \( \Delta U \) using Equation \( \ref{18.11} \), we need to calculate \( \Delta(PV) \). The process is carried out at a constant pressure of 1.00 atm, so

\[
\begin{align*}
\Delta(PV) &= P\Delta V = P(V_f - V) = (1.00\text{ atm})(0.0180\text{ L} - 0.0197\text{ L}) \\
&= (-1.7 \times 10^{-3}\text{ L atm})(101.3\text{ J L atm}^{-1}) = -0.0017\text{ J}
\end{align*}
\]

C. Substituting the calculated values of \( \Delta H \) and \( P\Delta V \) into Equation 18.11,

\[ \Delta U = \Delta H - P\Delta V = 6010\text{ J} - (-0.0017\text{ J}) = 6010\text{ J} = 6.01 \text{ kJ} \]

**Exercise \( \PageIndex{1} \)**

At 298 K and 1 atm, the conversion of graphite to diamond requires the input of 1.850 kJ of heat per mole of carbon. The molar volumes of graphite and diamond are 0.00534 L and 0.00342 L, respectively. Calculate \( \Delta H \) and \( \Delta U \) for the
The conversion of C (graphite) to C (diamond) under these conditions.

**Answer a**

\[ \Delta H = 1.85 \text{ kJ/mol} \]

**Answer b**

\[ \Delta U = 1.85 \text{ kJ/mol} \]

### The Relationship between ΔH and ΔU

If ΔH for a reaction is known, we can use the change in the enthalpy of the system (Equation \(\text{(5.3.5)}\)) to calculate its change in internal energy. When a reaction involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably (ΔV = 0). Under these conditions, we can simplify Equation \(\text{(5.3.5)}\) to ΔH = ΔU. If gases are involved, however, ΔH and ΔU can differ significantly. We can calculate ΔU from the measured value of ΔH by using the right side of Equation \(\text{(5.3.5)}\) together with the ideal gas law, PV = nRT. Recognizing that Δ(PV) = Δ(nRT), we can rewrite Equation \(\text{(5.3.5)}\) as follows:

\[ \Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) \]

At constant temperature, Δ(nRT) = RTΔn, where Δn is the difference between the final and initial numbers of moles of gas. Thus

\[ \Delta U = \Delta H - RT\Delta n \]

For reactions that result in a net production of gas, Δn > 0, so ΔU < ΔH. Conversely, endothermic reactions (ΔH > 0) that result in a net consumption of gas have Δn < 0 and ΔU > ΔH. The relationship between ΔH and ΔU for systems involving gases is illustrated in Example \(\PageIndex{2}\).

For reactions that result in a net production of gas, ΔU < ΔH. For endothermic reactions that result in a net consumption of gas, ΔU > ΔH.

**Example \(\PageIndex{2}\): The Relationship Between ΔH and ΔU in Gas Evolving Reactions**

The combustion of graphite to produce carbon dioxide is described by the equation

\[ C_{(\text{graphite, s})} + O_{2(g)} \rightarrow CO_{2(g)} \]

At 298 K and 1.0 atm, ΔH = −393.5 kJ/mol of graphite for this reaction, and the molar volume of graphite is 0.0053 L. What is ΔU for the reaction?

**Given**: balanced chemical equation, temperature, pressure, ΔH, and molar volume of reactant

**Asked for**: ΔU

**Strategy**: 
A. Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.

B. Substitute this value and the data given into Equation $\ref{5.3.7}$ to obtain $\Delta U$.

**SOLUTION**

A In this reaction, 1 mol of gas (CO$_2$) is produced, and 1 mol of gas (O$_2$) is consumed. Thus $\Delta n = 1 - 1 = 0$.

B Substituting this calculated value and the given values into Equation $\ref{5.3.7}$,

$$\Delta U = \Delta H - RT\Delta n = (-393.5 \text{ kJ/mol}) - [8.314 \text{ J/(mol·K)}](298 \text{ K})(0)$$

$$= (-393.5 \text{ kJ/mol}) - (0 \text{ J/mol}) = -393.5 \text{ kJ/mol}$$

To understand why only the change in the volume of the gases needs to be considered, notice that the molar volume of graphite is only 0.0053 L. A change in the number of moles of gas corresponds to a volume change of 22.4 L/mol of gas at standard temperature and pressure (STP), so the volume of gas consumed or produced in this case is $(1)(22.4 \text{ L}) = 22.4 \text{ L}$, which is much, much greater than the volume of 1 mol of a solid such as graphite.

Exercise $\PageIndex{2}$

Calculate $\langle \Delta U \rangle$ for the conversion of oxygen gas to ozone at 298 K:

$$3\text{O}_2(\text{g}) \rightarrow 2\text{O}_3(\text{g}).$$

The value of $\langle \Delta H \rangle$ for the reaction is 285.4 kJ.

**Answer**

$$288 \text{ kJ}$$

As Example $\PageIndex{2}$ illustrates, the magnitudes of $\Delta H$ and $\Delta U$ for reactions that involve gases are generally rather similar, even when there is a net production or consumption of gases.

**Summary**

Enthalpy is a state function, and the change in enthalpy of a system is equal to the sum of the change in the internal energy of the system and the PV work done. Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure. The change in the internal energy of a system is the sum of the heat transferred and the work done. At constant pressure, heat flow (q) and internal energy (U) are related to the system’s enthalpy (H). The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for $\Delta U$. 

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