When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. Enthalpy ($H$) is the sum of the internal energy ($U$) and the product of pressure and volume ($PV$) given by the equation:

$$H = U + PV$$

When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. Enthalpy is a state function which depends entirely on the state functions ($T$, $P$, and $U$). Enthalpy is usually expressed as the change in enthalpy (\(\Delta H\)) for a process between initial and final states:

$$\Delta H = \Delta U + \Delta PV$$

If temperature and pressure remain constant through the process and the work is limited to pressure-volume work, then the enthalpy change is given by the equation:

$$\Delta H = \Delta U + P\Delta V$$

Also at constant pressure the heat flow ($q$) for the process is equal to the change in enthalpy defined by the equation:

$$\Delta H = q$$

By looking at whether $q$ is exothermic or endothermic we can determine a relationship between \(\Delta H\) and \(q\). If the reaction absorbs heat it is endothermic meaning the reaction consumes heat from the surroundings so \(q > 0\) (positive). Therefore, at constant temperature and pressure, by the equation above, if $q$ is positive then \(\Delta H\) is also positive. And the same goes for if the reaction releases heat, then it is exothermic, meaning the system gives off heat to its surroundings, so \(q < 0\) (negative). If \(q\) is negative, then \(\Delta H\) will also be negative.

### Enthalpy Change Accompanying a Change in State

When a liquid vaporizes the liquid must absorb heat from its surroundings to replace the energy taken by the vaporizing molecules in order for the temperature to remain constant. This heat required to vaporize the liquid is called enthalpy of vaporization (or heat of vaporization). For example, the vaporization of one mole of water the enthalpy is given as:

$$\Delta H = 44.0 \text{ kJ at 298 K}$$

When a solid melts, the required energy is similarly called enthalpy of fusion (or heat of fusion). For example, one mole of ice the enthalpy is given as:

$$\Delta H = 6.01 \text{ kJ at 273.15 K}$$

Enthalpy can also be expressed as a molar enthalpy, \(\Delta H_m\), by dividing the enthalpy or change in enthalpy by the number of moles. Enthalpy is a state function. This implies that when a system changes from one state to another, the change in enthalpy is independent of the path between two states of a system.
If there is no non-expansion work on the system and the pressure is still constant, then the change in enthalpy will equal the heat consumed or released by the system (q). \[
\Delta H = q \tag{2}
\]

This relationship can help to determine whether a reaction is endothermic or exothermic. At constant pressure, an endothermic reaction is when heat is absorbed. This means that the system consumes heat from the surroundings, so \( q \) is greater than zero. Therefore according to the second equation, the \( \Delta H \) will also be greater than zero. On the other hand, an exothermic reaction at constant pressure is when heat is released. This implies that the system gives off heat to the surroundings, so \( q \) is less than zero. Furthermore, \( \Delta H \) will be less than zero.

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**Effect of Temperature on Enthalpy**

When the temperature increases, the amount of molecular interactions also increases. When the number of interactions increase, then the internal energy of the system rises. According to the first equation given, if the internal energy \( (U) \) increases then the \( \Delta H \) increases as temperature rises. We can use the equation for heat capacity and Equation 2 to derive this relationship.

\[
C = \frac{q}{\Delta T} \tag{3}
\]

Under constant pressure, substitute Equation \( \text{ref}(2) \) into Equation \( \text{ref}(3) \):

\[
C_p = \left( \frac{\Delta H}{\Delta T} \right)_P \tag{4}
\]

where the subscript \( (P) \) indicates the derivative is done under constant pressure.

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**The Enthalpy of Phase Transition**

Enthalpy can be represented as the standard enthalpy, \( \Delta H^0 \). This is the enthalpy of a substance at standard state. The standard state is defined as the pure substance held constant at 1 bar of pressure. Phase transitions, such as ice to liquid water, require or absorb a particular amount of standard enthalpy:

- **Standard Enthalpy of Vaporization** \( (\Delta H_{\text{vap}}^0) \) is the energy that must be supplied as heat at constant pressure per mole of molecules vaporized (liquid to gas).
- **Standard Enthalpy of Fusion** \( (\Delta H_{\text{fus}}^0) \) is the energy that must be supplied as heat at constant pressure per mole of molecules melted (solid to liquid).
- **Standard Enthalpy of Sublimation** \( (\Delta H_{\text{sub}}^0) \) is the energy that must be supplied as heat at constant pressure per mole of molecules converted to vapor from a solid.

\[
\Delta H_{\text{sub}}^0 = \Delta H_{\text{fus}}^0 + \Delta H_{\text{vap}}^0
\]

The enthalpy of condensation is the reverse of the enthalpy of vaporization and the enthalpy of freezing is the reverse of the enthalpy of fusion. The enthalpy change of a reverse phase transition is the negative of the enthalpy change of the forward phase transition. Also the enthalpy change of a complete process is the sum of the enthalpy changes for each of the phase transitions incorporated in the process.
Outside Links


References

1. Atkins, Peter and de Paula, Julio; Physical Chemistry for the Life Sciences, United States, 2006. Katherine Hurley

Problems

1. Calculate the enthalpy (ΔH) for the process in which 45.0 grams of water is converted from liquid at 10° C to vapor at 25° C.

Solution

Part 1: Heating water from 10.0 to 25.0 °C

\[ \Delta kJ = 45.0 \text{g H}_2\text{O} \times (4.184 \text{J/gH}_2\text{O °C}) \times (25.0 - 10.0) \text{°C} \times 1 \text{kJ}/1000 \text{J} = 2.82 \text{kJ} \]

Part 2: Vaporizing water at 25.0 °C

\[ \Delta kJ = 45.0 \text{ g H}_2\text{O} \times 1 \text{ mol H}_2\text{O}/18.02 \text{ g H}_2\text{O} \times 44.0 \text{kJ}/1 \text{ mol H}_2\text{O} = 110 \text{kJ} \]

Part 3: Total Enthalpy Change

\[ \Delta H = 2.82 \text{kJ} + 110 \text{kJ} \]

Contributors

- Katherine Hurley (UCD), Jennifer Shamieh (UCD)