

2.4: Enthalpy

Enthalpy

A Definition

In the previous section, we discussed several different process conditions, focusing first on isothermal expansions and contractions, and then on adiabatic, constant-volume calorimetry. In this section we will focus on constant pressure processes so that we can study the thermodynamic property enthalpy, H . Recall the definition of internal energy

$$U = q + w \quad (2.4.1)$$

Under constant volume conditions, the system could do no work, so

$$U = q_V \quad (2.4.2)$$

If the volume of the system is allowed to change, however, the system can do work as it expands against the external pressure, w will have a negative, non-zero value, and

$$U < q \quad (2.4.3)$$

Equation 2.4.1 can be rewritten as

$$U = q + (-PV) \quad (2.4.4)$$

where $w = -PV$ is always be negative if the system is constrained to do only expansion work.

Enthalpy (H) is defined as the sum of the internal energy (U) and the product of pressure and volume (PV):

$$H = U + PV \quad (2.4.5)$$

Enthalpy is a state function which depends entirely on the state functions V , P and U . It is not possible to measure absolute enthalpy, but the change in enthalpy (ΔH) for a process between initial and final states can be measured experimentally:

$$\Delta H = \Delta U + \Delta PV \quad (2.4.6)$$

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:

$$\Delta H = \Delta U + P\Delta V \quad (2.4.7)$$

Note

Equation 2.4.7 can be derived starting with the basic premise of an infinitesimal change to the system:

$$H + dH = (U + dU) + (P + dP)(V + dV) \quad (2.4.8)$$

$$H + dH = U + dU + PV + VdP + PdV + dPdV \quad (2.4.9)$$

The VdP term is 0 because the process is carried out at constant pressure. The $dPdV$ term is so small (the product of two infinitesimal changes) that it can be approximated as 0. Thus Equation 2.4.9 becomes

$$H + dH = U + dU + PV + PdV \quad (2.4.10)$$

By the definition of Equation 2.4.5, $H = U + PV$, thus

$$H + dH = H + dU + PdV \quad (2.4.11)$$

which becomes

$$dH = dU + PdV \quad (2.4.12)$$

If the system undergoes a change from a fixed initial condition to a fixed final condition, then

$$\int dH = \int dU + P \int dV \quad (2.4.13)$$

resulting in

$$\Delta H = \Delta U + P\Delta V \quad (2.4.14)$$

Per the definition of the first law,

$$\Delta U = q + w \quad (2.4.15)$$

Because the constant-pressure work will always be expansion work against the surroundings, $w = -P\Delta V$, and

$$\Delta H = q_P + (-P\Delta V) + P\Delta V \quad (2.4.16)$$

We now can see that the change in enthalpy is the change in heat at constant pressure:

$$\Delta H = q_P \quad (2.4.17)$$

Example 2.4.1: Enthalpy Change Accompanying a Change in State

When a liquid vaporizes, the temperature remains constant because the liquid absorbs heat from its surroundings to replace the energy taken in by the vaporizing molecules as the intermolecular forces are broken. This heat required to vaporize the liquid is called **enthalpy of vaporization** (or heat of vaporization).

Suppose that a sample of methanol is heated to its boiling point at a constant pressure of 1.00 atm. An electric current of 0.750 amps from a 12.0 Volt power supply is passed through a coil for 250 seconds to add heat to the liquid. If 1.88 grams of methanol is converted to vapor by this process, what is the ΔH for this specific process, what is the ΔH_m for methanol?

Strategy: Use the Equation $q = I \cdot t \cdot \Delta\phi$ to calculate the energy used to vaporize the liquid, which is ΔH , and then divide by the number of moles to determine the molar enthalpy of vaporization.

Answer

$$q_P = \Delta H = (0.750 \frac{C}{s})(250s)(12.0 \frac{J}{C}) = 2250 J$$

$$\Delta H_m = \left(\frac{2250 J}{1.88 \text{ grams}} \right) \left(\frac{32.0 \text{ grams}}{1.00 \text{ mole}} \right) \left(\frac{1.00 \text{ kJ}}{1000 J} \right) = 38.3 \frac{\text{kJ}}{\text{mole}}$$

Exercise 2.4.1

Suppose that a sample of water is heated to its boiling point at a constant pressure of 1.00 atm. An electric current of 0.850 amps from a 12.0 Volt power supply is passed through a coil for 150 seconds to add heat to the liquid. If 1.88 grams of water is converted to vapor by this process, what is the ΔH for this specific process, what is the ΔH_m for methanol?

Answer: $\Delta H = 1530 \text{ J}$, $\Delta H_m = 40.7 \frac{\text{kJ}}{\text{mole}}$

Constant Pressure Calorimetry

It is relatively easy to measure an enthalpy change for a chemical or physical change that occurs at constant pressure. Often an insulated container such as a Styrofoam™ cup can be used as the reaction vessel, with the atmosphere exerting the constant pressure. This type of calorimeter is called an **isobaric** calorimeter. A bomb calorimeter can be used to find ΔH for reactions involving solids and liquids because the molar volumes of solids and liquids are relatively small, leading to $\Delta H \approx \Delta U$. ΔH may differ greatly from ΔU for processes involving gases because of the large molar volumes of gases. For a reaction that involves a change in the number of moles of perfect gases Δn_g , under isothermal conditions,

$$\Delta H = \Delta U + \Delta n_g RT \quad (2.4.18)$$

Example 2.4.2: ΔH vs. ΔU

A) Solids

Calculate the difference between the ΔH_m and the ΔU_m for the conversion of graphite to diamond when the pressure is 1.0 bar. The density of graphite is $2.15 \frac{\text{grams}}{\text{cm}^3}$ and the density of diamond is $3.51 \frac{\text{grams}}{\text{cm}^3}$.

Strategy: You will need to use Equation 2.4.7 to solve this problem, with the understanding that ΔV_m can be found by dividing the molar mass M by the density ρ .

First, rearrange the Equation $\Delta H_m = \Delta U_m + P\Delta V_m$ to $\Delta H_m - \Delta U_m = P\Delta V_m$.

Next, realize that $\Delta V_m = V_{m, \text{diamond}} - V_{m, \text{graphite}}$

and therefore $\Delta V_m = \frac{M_{\text{carbon}}}{\rho_{\text{diamond}}} - \frac{M_{\text{carbon}}}{\rho_{\text{graphite}}}$

Answer: $\Delta H_m - \Delta U_m = P \left(\frac{M_{\text{carbon}}}{\rho_{\text{diamond}}} - \frac{M_{\text{carbon}}}{\rho_{\text{graphite}}} \right) = PM \left(\frac{1}{\rho_{\text{diamond}}} - \frac{1}{\rho_{\text{graphite}}} \right)$

$$\Delta H_m - \Delta U_m = (1.0 \times 10^5 \text{ Pa}) \times (12.01 \frac{\text{grams}}{\text{mole}}) \times \left(\frac{1.00 \text{ cm}^3}{3.51 \text{ grams}} - \frac{1.00 \text{ cm}^3}{2.15 \text{ gram}} \right) \times \left(\frac{1.00 \text{ m}^3}{1.00 \times 10^6 \text{ cm}^3} \right) \times \left(\frac{1.00 \text{ J}}{1.00 \text{ Pa} \cdot \text{m}^3} \right)$$

$$= -0.22 \frac{\text{J}}{\text{mole}}$$

This is a small fraction of ΔH_m for the process, which is +1.9 kJ.

B) Gases

Calculate the difference between the ΔH_m and the ΔU_m for the reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ at 298 K.

Strategy: Use Equation 2.4.18 to solve for $\Delta H_m - \Delta U_m = \Delta n_g RT$

Answer: $\Delta H_m - \Delta U_m = (-1 \text{ mole}) \times 0.008314 \frac{\text{kJ}}{\text{mole} \cdot \text{K}} \times (298 \text{ K}) = -2.48 \text{ kJ}$

Notice that the difference between ΔH and ΔU is much greater for a reaction involving the change in the number of moles of gases than it is for a phase change involving different solid forms of an element.

Exercise 2.4.2

A. Calculate the difference between the ΔH_m and the ΔU_m for the conversion of white phosphorus to black phosphorus when the pressure is 1.0 bar. The density of white phosphorus is $1.82 \frac{\text{grams}}{\text{cm}^3}$ and the density of black phosphorus is $2.69 \frac{\text{grams}}{\text{cm}^3}$.

Answer: $-0.55 \frac{\text{J}}{\text{mole}}$

B. Calculate the difference between the ΔH_m and the ΔU_m for the reaction $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{s})$ at 298 K.

Answer: -4.96 kJ

The Relationship between Enthalpy and Temperature

It is often assumed that the enthalpy of a substance or a reaction is constant over a small range of temperatures. While this assumption is true, it is possible to calculate how much the enthalpy changes as the temperature changes. The manner in which the enthalpy varies as the temperature changes depends on whether the process is carried out under constant pressure or constant volume conditions.

ΔH vs. ΔT at Constant Pressure

The enthalpy of most systems increases as the temperature increases, and so a plot of enthalpy versus temperature results in a graph with a positive slope at any point. Each instantaneous slope is defined as the **heat capacity at constant pressure**, C_P . In other words,

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (2.4.19)$$

As with the described in the derivation of the heat capacity at constant volume, C_V , Equation 2.4.19 is a partial derivative because the enthalpy of a system will typically vary with both pressure and temperature, but we are holding the pressure constant and allowing only the temperature to change.

Because C_P tells us the amount of heat needed to change the temperature of a sample of a substance at constant pressure, we can also say that an infinitesimal change in enthalpy is equal to an infinitesimal change in temperature multiplied by the heat capacity at constant pressure

$$dH = C_P dT \quad (2.4.20)$$

If the heat capacity of the substance does not change a great deal over the temperature range of interest, then the slope of the H versus T graph will be fairly constant. In this case

$$\Delta H = \int C_P dT = C_P \cdot (T_2 - T_1) = C_P \cdot \Delta T \quad (2.4.21)$$

As noted in Equation 2.4.17,

$$\Delta H = q_P \quad (2.2.17)$$

so that

$$q_P = C_P \cdot \Delta T \quad (2.4.22)$$

Equation 2.4.22 shows us that we can experimentally determine the constant pressure heat capacity of a substance fairly easily by measuring the change in temperature of a substance as heat is added to it under constant pressure conditions.

The value of C_P is an extensive property because it tells us how much heat is needed to change the temperature of that specific sample of the pure substance. We can determine the intensive property of this pure substance, the molar heat capacity at constant pressure, $C_{P,m}$, if we divide the experimentally obtained C_P by the number of moles of the substance used in the experiment:

$$C_{P,m} = \frac{C_P}{n} \quad (2.4.23)$$

We can also calculate a second intensive property, the specific heat capacity, $C_{P,s}$, which is the heat capacity per mass of sample:

$$C_{P,s} = \frac{C_P}{mass} \quad (2.4.24)$$

The value of C_P does actually change as the temperature changes. If it is necessary to estimate this change in value of C_P with a change in temperature, the following equation can be used:

$$C_{P,m} = a + bT + \frac{c}{T^2} \quad (2.4.25)$$

where the values of a, b, and c are temperature-independent and can be found in reference tables.

Example 2.4.3:

What is the change in molar enthalpy of CO_2 when it is heated from 20°C to 75°C ? For CO_2 $a = 44.22 \text{ J}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$, $b = 8.79 \times 10^{-3} \text{ J}\cdot\text{mole}^{-1}\cdot\text{K}^{-2}$, and $c = -8.62 \times 10^5 \text{ J}\cdot\text{mole}^{-1}\cdot\text{K}$.

Strategy: Because C_P changes as the temperature changes, we must use Equation 2.4.21:

$$\Delta H = \int C_P dT = C_P \cdot (T_2 - T_1) = C_P \cdot \Delta T \quad (2.2.21)$$

determine the integral and evaluate the result over the range of temperatures.

$$\text{Answer: } \Delta H_m = \int \left(a + bT + \frac{c}{T^2} \right) dT = H_m(T_2) - H_m(T_1) = a(T_2 - T_1) + \frac{1}{2}b(T_2^2 - T_1^2) - c \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\begin{aligned} H_m(348\text{K}) - H_m(293\text{K}) &= 44.22 \frac{\text{J}}{\text{mole}\cdot\text{K}} (348\text{K} - 293\text{K}) + \frac{1}{2} \left(0.00879 \frac{\text{J}}{\text{mole}\cdot\text{K}^2} \right) [(348\text{K})^2 - (293\text{K})^2] \\ &- \left(-862,000 \frac{\text{J}\cdot\text{K}}{\text{mole}} \right) \left(\frac{1}{348\text{K}} - \frac{1}{293\text{K}} \right) = 2120 \frac{\text{J}}{\text{mole}} = 2.12 \frac{\text{kJ}}{\text{mole}} \end{aligned}$$

Exercise 2.4.3

What is the change in molar enthalpy of CO_2 when it is heated from 10°C to 125°C ? For CO_2 $a = 44.22 \text{ J}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$, $b = 8.79 \times 10^{-3} \text{ J}\cdot\text{mole}^{-1}\cdot\text{K}^{-2}$, and $c = -8.62 \times 10^5 \text{ J}\cdot\text{mole}^{-1}\cdot\text{K}$.

$$\text{Answer: } 4.55 \frac{\text{kJ}}{\text{mole}}$$

C_P vs. C_V

If the system of interest expands when heated under constant pressure conditions (as most systems do), then the system is doing work on the surroundings. In this case, less energy is acting to heat the system, and the temperature of the system increases less than it would if the system were held to a constant volume. A smaller increase in temperature indicates a higher heat capacity. Thus, in most cases, the constant pressure heat capacity is greater than the constant volume heat capacity,

$$C_P > C_V \quad (2.4.26)$$

For perfect gases

$$C_P - C_V = nR \quad (2.4.27)$$

Contributors and Attributions

- [Tom Neils](#) (Grand Rapids Community College)

2.4: [Enthalpy](#) is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.