

## 7.15: Defining Enthalpy, $H$

Any mathematical expression that involves only state functions must itself be a state function. We could define  $\Gamma = E^2 P^2 VT$ , and  $\Gamma$  would be a state function. However, it is not a useful state function. We can define several state functions that have the units of energy and that turn out to be particularly useful. One of them is named enthalpy and is customarily represented by the symbol  $H$ . We define **enthalpy**:

$$H = E + PV.$$

One reason that enthalpy is a useful state function emerges if we examine the change in  $H$  when the system pressure is equal to the applied pressure, and both are constant. (When these conditions are satisfied, we usually denote the heat accepted by the system as “ $q_P$ .”) If all of the work is pressure–volume work, we have

$$\begin{aligned}\Delta H &= \Delta E + P\Delta V \\ &= q_P + w + P\Delta V \\ &= q_P - P_{\text{applied}} \int dV + P\Delta V \\ &= q_P - (P_{\text{applied}} - P) \Delta V \\ &= q_P\end{aligned}$$

If these conditions are satisfied, the enthalpy change is the same thing as the heat added to the system. When we want to express the requirement that the system and applied pressures are equal and constant, we often just say that the process “occurs at a constant pressure.” This is another convenient figure of speech. It also reflects our expectation that the system pressure and the applied pressure will equilibrate rapidly in most circumstances.

For an ideal gas, the molar energy depends only on temperature. Since  $PV = RT$  for an ideal gas,  $PV$  depends only on temperature. Hence, the molar enthalpy of an ideal gas also depends only on temperature. For an ideal gas, we have the parallel relationships:

$$\left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial q}{\partial T}\right)_V = C_V$$

and

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial q}{\partial T}\right)_P = C_P$$

Earlier we asserted that, while energy is a state function, heat and work are not. **Hess’s law**, as originally formulated in 1840, says that the heat changes for a series of chemical reactions can be summed to get the heat change for the overall process described by the sum of the chemical reactions. This amounts to saying that heat is a state function. As it stands, this is a contradiction. The resolution is, of course, that Hess’s law was formulated for a series of chemical reactions that occur at the same constant pressure. Then the heat involved in each step is the enthalpy change for that step, and since enthalpy is a state function, there is no contradiction. Modern statements of Hess’s law frequently forego historical accuracy in favor of scientific accuracy to assert that the enthalpy change for a series of reactions can be summed to get the enthalpy change for the overall process. Thus revised, Hess’s law ceases to be a seminal but imperfect conjecture and becomes merely a special case of the principle that enthalpy is a state function.

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