

## 7.12: Notation for Changes in Thermodynamic Quantities - E vs. $\Delta E$

From the outset of our study of energy, we recognize that we are always dealing with energy changes. Even when we write  $E = E(P, T, h)$  to indicate that energy is a function of  $P$ ,  $T$ , and  $h$ , we recognize that  $E$  represents the energy difference between the state of the system characterized by  $P$ ,  $T$ , and  $h$  and the state of the system when the independent variables correspond to a reference state in which, by definition,  $E = 0$ . As we observe in §6-2, we can sort thermodynamic variables into two classes. Some, like  $P$ ,  $V$ , and  $T$ , can be measured only for a system. Others, like  $q$ ,  $w$ ,  $E$ ,  $S$ ,  $H$ ,  $G$ , and  $A$ , can be measured only for a process. To say that the volume of a system is one cubic meter has absolute significance. To say that the energy of a system is one joule means nothing unless we know the reference state.

When we intend to specify that the reference state for energy is the particular state specified by  $P = P_0$ ,  $T = T_0$ , and  $h = h_0$ , we write " $E(P_0, T_0, h_0) = 0$ ." Otherwise, when we write " $E = E(P, T, h)$ ," we could equally well write " $\Delta E = E(P, T, h)$ ." We intend either of these formulations to mean the same thing as " $E = E(P, T, h) - E(P_0, T_0, h_0)$  and  $E(P_0, T_0, h_0) = 0$ ."

Whether we write  $E$  or  $\Delta E$ , the quantity represented is the difference in energy between some initial and some final state. When we focus on very small changes, we can write  $dE$  or  $d(\Delta E)$ . If our perspective is that we are describing a process, we may prefer to write " $E$ "; if our perspective is that we are describing a change in the system, we may prefer to write " $\Delta E$ ." In practice, our choice depends primarily on what we have grown accustomed to in the context at hand. In the discussion above, we write  $E = q + w$ . We could equally well write  $\Delta E = q + w$ . The meaning is the same. We can make similar statements about most thermodynamic functions. Often there is no particular reason to prefer  $X$  over  $\Delta X$ , or *vice versa*.

However, there are circumstances in which the delta notation serves particular purposes. If a system undergoes a change in which some thermodynamic variables remain constant, the delta notation provides a convenient way to indicate that a particular variable is not constant. For example, if the volume of a system changes while the applied pressure remains constant, we write  $w = -P_{\text{applied}}\Delta V$ .

Similarly, we often want to describe processes in which some state functions are different in the final state than they are in the initial state, while other state functions are the same in both states, but not necessarily constant throughout the process. In the next few chapters, we develop properties of the state functions entropy,  $S$ , enthalpy,  $H$ , and Gibbs free energy,  $G$ . We define the Gibbs free energy by the relationship  $G = H - TS$ . To specify the relationship among the changes in these state functions when the final temperature is the same as the initial temperature, we write  $\Delta G = \Delta H - T\Delta S$ . Here too, we often say that this relationship relates the changes in  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  when "the temperature is constant." This is another useful, but potentially misleading, figure of speech. It is important to remember that the equation is valid for any path between the same two states, even if the temperature varies wildly along that path, so long as the initial and final states are at the same temperature.

Finally, we find it convenient to use subscripted versions of the delta notation to specify particular kinds of processes. For a process in which one mole of a pure substance vaporizes to its gas at a particular temperature, we write  $\Delta_{\text{vap}}H$  and  $\Delta_{\text{vap}}G$  to denote the changes in enthalpy and Gibbs free energy, respectively. (We can write  $\Delta_{\text{vap}}E$  to denote the change in the energy; however,  $\Delta_{\text{vap}}E$  is not a quantity that we find useful very often.) Similarly for the fusion and sublimation of one mole of a pure substance at a particular temperature, we write  $\Delta_{\text{fus}}G$ ,  $\Delta_{\text{sub}}G$ ,  $\Delta_{\text{fus}}H$ , and  $\Delta_{\text{sub}}H$ . We also find it convenient to write  $\Delta_rH$  and  $\Delta_rG$  to denote the changes in these quantities when a chemical reaction occurs. When we do so, it is essential that we specify the corresponding stoichiometric equation.

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