

Free Energy Worksheet

1. With certain assumptions, the *change* in the enthalpy ΔH may be defined as “the heat absorbed by a system under conditions of constant pressure.” (That is, if $\Delta H > 0$, heat is *absorbed* and enthalpy *increases*; if $\Delta H < 0$, heat is *given off* and enthalpy *decreases*.) Let’s see how ΔH is related to the internal energy U of a system.

- a) Write down the equation that expresses the first law of thermodynamics in the following form:

$$Q =$$

- b) In this discussion, will assume that the only work being done on the system is mechanical work, or “PdV” work. Then (under conditions of constant pressure), $W = P\Delta V$; rewrite the equation for Q in terms of ΔU , P and ΔV .

$$Q = \text{constant pressure}$$

- c) We should now have arrived at the expression $Q = \Delta U + P\Delta V$, which holds for constant-pressure conditions. This equation says that *heat absorbed* under constant pressure does two things: (1) increases the *internal energy (E)* of the system, and (2) allows the system to do mechanical work *on the surroundings*.

Using the definition that ΔH is *equal* to heat absorbed under constant pressure, write the equation from (b) in terms of ΔH , instead of Q :

$$\Delta H = \text{constant pressure}$$

So now we can see that when the enthalpy of a system *changes* by an amount ΔH (under conditions of constant pressure), there are actually *two* separate contributions to this change: (1) the change in the *internal energy* of the system (ΔU), and (2) the work done *by* the system *on* the surroundings ($P\Delta V$). An increase in internal energy, *or* positive work being done *by* the system, will both result in an increase in the enthalpy H of the system.

2. It would be useful to be able to predict whether a process can occur. We will try to find some property of the system that would allow us to make such a prediction. In order to do this, we will have to make use of the second law of thermodynamics.