

# Top Ten List of Most Common Thermodynamic Errors

In our experience, students are rarely creative, in terms of the thermodynamic errors they are likely to make. This is good news! It means that you can easily and significantly enhance your classroom performance, just by watching out for the common pitfalls listed below (as well as various others, all discussed in greater detail in *A Conceptual Guide to Thermodynamics*).

Heed our advice, and don't become another statistic on this list!

**Number 10:** *Using  $T$  and  $U$  in calorimetry applications, instead of  $\Delta T$  and  $\Delta U$ .* Since  $Q$  is not a state function, all state functions to which it is compared must get a ' $\Delta$ ' factor in front (see Number 3) below. Calorimetry is also a context in which system and surroundings are often confused.

**Number 9:** *Confusing the state of a single molecule with the molecular state of the whole system.* This can lead to incorrect expressions such as  $S = Nk \ln(\Omega)$ , and numerical results that are consequently off by a factor of around Avogadro's number!

**Number 8:** *Assuming that  $\Delta S > 0$  for a spontaneous irreversible change.* The Second Law states no such thing, except for the special case of *isolated* systems. Otherwise, it is  $\Delta S_{\text{tot}} > 0$ .

**Number 7:** *Neglecting to specify the constant variables in a thermodynamic change.* Even for the simplest of thermodynamic systems—i.e., a pure substance in a single phase—at least two independent variables are needed to uniquely specify a given change. A single modifier such as “isothermal,” “isobaric,” or “expansion” is therefore insufficient.

**Number 6:** *Assuming that  $P_{\text{sur}}(V)$  is a constant when computing  $W$ .* Only for *isobaric* processes can this simplifying assumption be made, leading to  $W = -P_{\text{sur}}\Delta V$  (see Number 4 below).

**Number 5:** *Assuming that  $P_{\text{sur}} = P$  when computing  $W$ .* Only for *reversible* processes can this simplifying assumption be made—although it is surprising how many books can be a bit sloppy on this point!

**Number 4:** *Getting the sign of  $W$  wrong.* The standard sign convention, encouraged by IUPAC, and used by scientists and some engineers, is to define  $W$  as the work done *on* the system *by* the surroundings,  $W = -\int P_{\text{sur}}(V) dV$ . As indicated, this convention requires an explicit minus sign, which students often forget. And of course, it does not help that some engineers define  $W = \int P_{\text{sur}}(V) dV \dots$

**Number 3:** *Combining  $X$ ,  $\Delta X$ , and  $dX$  in the same equation.* In any given expression, every term must have one ' $\Delta$ ' factor, one ' $d$ ' factor, or no such factors. As these represent macroscopic, infinitesimal, and no change, respectively, to combine them would be to compare apples with oranges.

**Number 2:** *Applying the ideal gas law to a condensed phase.* As an approximation, the ideal gas law is applicable to *gases only!* For liquids and solids, it is not even *remotely* correct.

**Number 1:** *The liter/cubic meter error.* Students often make this error when computing energy as pressure times volume. The SI unit of energy, i.e. the Joule (J) is equal to  $1 \text{ Pa m}^3$ , *not*  $1 \text{ Pa L}$ . Because this error is *so* common, you should always be on the lookout for results that are either 1000 times larger or smaller than they should be.