

### *The First and Second Laws combined*

We have seen that the First Law can be expressed as  $\Delta U = \Delta Q + \Delta W$  (see formula [2.1]) and that the Second Law can be expressed as  $\Delta S = \Delta Q/T$  (see formula [2.4]) or in a slightly different form also as  $\Delta Q = T\Delta S$ . If we now combine the two laws by substituting that the exchanged heat is equal to  $T\Delta S$  into the First Law equation we arrive at  $\Delta U = T\Delta S + \Delta W$ . This can be rearranged into  $\Delta U - T\Delta S = \Delta W$ . We can draw two important conclusions from this. First, we know that for an isolated system  $\Delta U$  must be zero but also that  $\Delta S$  must be greater than zero ( $\Delta S > 0$ ). Suppose that for the sum of processes in the isolated system at 300K  $\Delta S = 10 \text{ J/K}$  then  $T\Delta S = 300 \times 10 = 3000 \text{ J}$ . Thus  $\Delta W = -3000 \text{ J}$  (the minus sign indicates that we can obtain within the system a *net* amount of useful work). Of course for a process in a certain part of the system we can have conditions (by burning fuel for instance) such that we can obtain more than 3000J of work, but that needs then to be compensated by other processes in another part of the system such that the sum will give us again 3000J for  $\Delta W$  or 10 J/k for  $\Delta S$  and  $\Delta U = 0$ , no escape possible! Second, at constant temperature, the term  $\Delta U - T\Delta S$  can be rearranged into  $\Delta(U-TS)$  and therefore:  $\Delta(U-TS) = \Delta W$ . What does this abracadabra bring us you will ask? The term  $U-TS$  is called “free energy”, also often called “available energy” in older literature. Now we see why we call it *available* energy since it is this amount of the total energy that is maximal *available* to perform work.

(If you read the reference materials in the back of the book, you’ll come across two more thermodynamic laws: the Zeroth Law and the Third Law. For the purpose of this book we do not need to concern ourselves with them, but if you’re really curious, you can read about them in Appendix I.)

### **Perpetual motion and engines**

Since the 11<sup>th</sup> century, many people have tried to beat the First Law with ingenious machines. There are good reasons for trying: if you could build a machine that could work forever without needing energy, that would solve the world’s energy problem in one stroke. You would gain immeasurable wealth, fame, and surely the Nobel Prize as well.