An Equation for the Second Law of Thermodynamics

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The second law of thermodynamicsis is usually stated in the form "the entropy of a closed system tends to increase", but as Jaynes has eloquently described there are many other equivalent forms [1]. This paper discusses a form that is particularly useful for molecular biology.

Tolman [2], says on page 546: "the well-known thermodynamic [relation] ..."

$$\Delta S \geq \int \frac{dQ}{T}$$

"...give[s] a general formulation of the second law" and again on page 558: "For our purposes we may regard the content of the ordinary second law of thermodynamics as given by the expression

$$\Delta S \geq \int \frac{\delta Q}{T} \tag{130.1}$$

which states that the increase in the entropy of a system, when it changes from one condition to another, cannot be less than the integral of the heat

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absorbed divided for each increment of heat by the temperature of a heat reservoir appropriate for supplying the increment in question. The equality sign in this expression is to be taken as applying to the limiting case of reversible changes." Further down Tolman does an integration of the statistical mechanical equivalent differential form to obtain the statistical mechanics equivalent of (130.1). The equation used in the second molecular machine paper [3, 4]:

$$dS \geq \frac{dQ}{T}$$

is also a differential form which when integrated gives equation (130.1) (ignoring the partial as Tolman did). This integration is the first step to obtaining the form useful for molecular machines. You may also find it useful also to read pages 48 through 55 of Fermi's clear writing on the topic [5] and the enlightening discussion on the many alternative forms of the Second law by Jaynes [1].

In Tolman's lucid explanation of the equation, given above, the equation refers to the *change* from one condition to another.

1. Note also that there is no problem at all integrating with a constant temperature since entropy is a state function.

2. Note further that it is the temperature of the heat supplied by the heat bath, *not that of the system*, which is appropriate in the above equations so apparently the temperature of the molecule actually doesn't matter for this step.

3. Finally, note Waldram's [6] use of a definition of entropy which *does not require equilibrium* (page 39, equation 4.3). Thus the application of this equation to a molecular system *which loses energy at constant temperature* is quite appropriate.

Using the equation to derive a familiar form of the Second Law

Consider two systems 1 and 2 that are adiabatically isolated from everything else. We allow some heat to flow from one system to the other. So we have

$$dS_1 \geq \frac{dq_1}{T} \tag{1}$$

and

$$dS_2 \geq \frac{dq_2}{T}. \tag{2}$$

Then the total entropy change is:

$$dS_{\text{total}} = dS_1 + dS_2 \tag{3}$$

so substituting from equation (1) and (2) into (3), we have

$$dS_{\text{total}} \geq \frac{dq_1}{T} + \frac{dq_2}{T} = \frac{dq_1 + dq_2}{T} = 0 \tag{4}$$

since the heat flow out of one equals that into the other ($dq1 = -dq2$). Hence the formulation

$$dS \geq \frac{dq}{T} \tag{5}$$

leads to the statement that the total entropy increase of an adiabatically isolated system is greater than or equal to zero. Note that this formulation in itself does NOT require isolation!

$dS \geq dq/T$ carries the content of the Second Law, as Tolman said.

Here is a similar argument from Fermi, page 56 [5]:

"As the first example, we consider the exchange of heat by thermal conduction between two parts, A_1 and A_2, of a system. Let T_1 and T_2 be the temperatures of these two parts, respectively, and let $T_1 < T_2$. Since heat flows by conduction from the hotter body to the colder body, the body A_2 gives up a quantity of heat Q which is absorbed by the body A_1. Thus, the entropy A_1 changes by an amount Q/T_1, while that of A_2 changes by the amount $-Q/T_2$. The total variation in entropy of the complete system is, accordingly,

$$\frac{Q}{T_1} - \frac{Q}{T_2}. \tag{6}$$

Since $T_1 < T_2$, this variation is obviously positive, so that the entropy of the entire system has been increased."

References

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