The third law of thermodynamics

R. M. Kiehn

Emeritus, Physics Dept., Univ. Houston
01/15/2003
rkiehn2352@aol.com

Abstract

From a topological point of view, the first law of thermodynamics is a cohomological statement that the difference between two non-exact 1-forms of heat Q and work W is a perfect differential, dU. The third law is a cohomological statement that the difference between two 3-forms Q^dQ and W^dW is a perfect differential, d(U^dW). Such concepts apply to irreversible thermodynamic processes.

1 Introduction

For physical systems that admit description in terms of a 1-form of Action, A, on a variety, it has been determined that the transport of the physical system along the flow lines generated by a vector field V can be described by the action of the Lie differential with respect to V acting on the 1-form, A. All Hamiltonian systems, for example, are subsets of such a description. Evolutionary process described by these methods are independent from the topological constraints of metric and connection that might be imposed upon the variety. The methods are of a topological nature, that calls to the forefront the topological fondations inherent in thermodynamics.

The format of the Lie differential acting on a 1-form, A,

$$L_{(V)}A = i(V)dA + d(i(V)A), \tag{1}$$

can be identified formally with the first law of thermodynamics:

$$\begin{aligned} L_{(V)}A &= W + dU = Q, & (2)\\ \text{where } W &= i(V)dA, & (3)\\ \text{and } U &= i(V)A, & (4) \end{aligned}$$

The statement emphasizes that the first law is a statement of topological cohomology; i.e., the difference between the non-exact 1-form of heat, Q, and the

1-form of work, W, is a perfect differential of the internal energy, U.

$$\text{Cohomological form of the First Law:}\quad Q - W = dU \tag{5}$$

This topological statement does not depend upon metric or connection.

It follows (by exterior differentiation of the first law) that

$$dQ - dW = 0. \tag{6}$$

It then is possible by exterior multiplication to compose a cohomological statement such that the difference between two fundamental 3-forms is also a perfect differential. This cohomological statement defines the third law of thermodynamics:

$$\text{The third law of thermodynamics:}\quad Q\hat{}dQ - W\hat{}dW = d(U\hat{}dW) \tag{7}$$

For Hamiltonian extremal or symplectic processes, it has been shown by Cartan that $dW = 0$. The statement is equivalent to the concept that the Pfaff dimension of W is 1. From the third law, it follows that for such processes, $Q\hat{}dQ \Rightarrow 0$; but if the 1-form Q is of Pfaff dimension 2, or less, then the process V, transporting the 1-form A, is thermodynamically reversible. All Hamiltonian and symplectic processes (such that $dW = 0$) are thermodynamically reversible.

The implication for reversible processes is that Q admits an integrating factor such that $Q = TdS$, thereby defining the concept of Temperature and Entropy. For reversible processes, the requirement that $Q\hat{}dQ \Rightarrow 0$, does not imply that W be of Pfaff dimension 1. In other words, reversible processes need not be Hamiltonian. The third law demonstrates that for all reversible processes:

$$\{W + dU\}\hat{}dT\hat{}dS \Rightarrow 0. \tag{8}$$

Then either the Work is the negative differential of the internal energy (which implies the process V is Hamiltonian relative to the Action 1-form A), or the sum of the Work and the differential of the Internal energy consists of terms that depend only upon the differentials of entropy and temperature:

$$W = TdS + B(T)dT - dU. \tag{9}$$

It follows that the Pfaff dimension of the Work 1-form can be 3, or less, and the process V still represents a thermodynamically reversible process.

If the Work 1-form is of Pfaff dimension 4, then it is impossible for the Heat 1-form to be of Pfaff dimension 2, or less. Hence processes that create a Work 1-form that is of Pfaff dimension 4 must be thermodynamically irreversible processes. The variety of functions that serves as a base for the exterior differential forms and the process must be of topological dimension of 4 or more, if the process acting on the physical system is thermodynamically irreversible.

The result is a theorem:

Theorem 1 *Irreversible evolution is an artifact of Pfaff dimension 4.*