

# A Brief History of Thermodynamics Notation

Rubin Battino\*

Department of Chemistry, Wright State University, Dayton, OH 45435

Laurence E. Strong

Department of Chemistry, Earlham College, Richmond, IN 47374

Scott E. Wood

Department of Chemistry, Illinois Institute of Technology, Chicago, IL 60616

One of us was recently asked, "I understand the use of  $H$  for enthalpy since that is *heat* related, but where does  $S$  for entropy come from?" We were stumped and decided to do some historical research to track down not only the origin of  $S$ , but also the other principal thermodynamic notation. In modern usage ( $I$ ) these are  $U$  (or  $E$ ) for energy (or internal energy),  $H$  for enthalpy,  $G$  for Gibbs energy,  $A$  for Helmholtz energy,  $S$  for entropy,  $W$  for work,  $Q$  for heat,  $T$  for temperature,  $P$  for pressure, and  $V$  for volume. (We will not discuss other symbols.)

With respect to  $U$ ,  $H$ ,  $G$ ,  $A$ , and  $S$ , where it is only possible to determine changes, we prefer to use the word "function". These state functions are derived from *exact* differentials. (The standard state implicit in the third law permits the calculation of "absolute" entropies, but we still regard the entropy as a function.) Since  $Q$  and  $W$  are determined by the integration of *inexact* differentials, we prefer to use the words *heat effects* and *work effects*.

The directly measurable properties of temperature, pressure, and volume have their symbols directly related to their origins and common usage. Temperature,  $T$ , naturally comes from the Latin *temperatura* or the French *temperature*. Pressure,  $P$ , comes from the Latin *pressura*. Volume,  $V$ , comes from the Greek and Latin *volumen*, which meant a "roll" of writing and, in our terms, the space that roll of writing occupied.

Work,  $W$ , appears to come from the Middle English *work*, *werk*, or *weorc*; and the related Anglo-Saxon *worc*, *werc*, and *weorc*. Heat,  $Q$ , is not directly related to the Middle English *hete* and *haete*, the Greek *hāetu* and *hāeto*, the Old High German *heiza* and *hizza*, the German *Hitze*, or the Danish *hitte*, to mention a few that all start with "H." At one point it became necessary to distinguish between heat effects which were symbolized as  $Q$  (probably taken from the French *calorique* and related to the caloric theory of heat) and the enthalpy symbolized as  $H$  (defined as  $U + PV$ ). The name "enthalpy" comes from the Greek *ενθαλπειν*, which means "to heat". Clausius in 1834 was using  $Q$  for heat, and this appeared to be a common usage at the time. Gibbs use  $\chi$  for the enthalpy and Epstein used a bold-face capital  $X$ .

We can quote Mendoza (2) to good effect on confusions surrounding the term "heat":

In fact, there are *two* heat quantities that it is useful to define. One is conserved in any reversible process, whether work is done or not—in modern terms, the entropy; the other is conserved by a body in adiabatic calorimetry—in modern terms, the quantity of heat or heat energy. Neither quantity is more fundamental than the other. It is through an historical accident, an arbitrary choice, that we happen to call one of these quantities by

the familiar term "heat" and the other by a pseudo-Greek name. In the early nineteenth century the two were confused. The writers of that time also had two names for the heat available, but when we read *any* paper of that period, "quantity of heat" and "quantity of caloric" must each be construed to mean sometimes "change of entropy" and sometimes "quantity of heat." Carnot himself stated explicitly that he used the two terms interchangeably; in fact, he had a tendency to reserve the term "caloric" for situations where we would now talk of entropy. For example, he usually wrote that in a reversible heat-engine, the amounts of caloric absorbed by the working substance at the high temperature and lost at the low were compensated.

Mendoza attributes this confusion to the poor experimental data that were available at the time.

This confusion wasn't really resolved until Clausius (3) defined entropy in his great paper of 1865. Professor E. Wilhelm has kindly provided us with a translation of part of p 390 of Clausius's paper.

If one searches for appropriate name for  $S$ , one could—similar to naming the quantity  $U$  the *heat content* and *work content* of a body—call the quantity  $S$  transformation content of a body. However, I think it is better to take the names of quantities so important for science from the ancient languages, because they can then be used unchanged in all modern languages. I propose to call the quantity  $S$ , according to the Greek word  $\eta'$  τροπή' = The change (transformation, transmutation), the *entropy* of a body.

So, in German he called it the *Entropie*, based on the Greek word meaning transformation or turning. So the entropy represented the "transformation-contents" (*Verwandlungsinhalt*) of a system. For this new function related to  $DQ/T$ , he used the symbol  $S$ , but it is not clear why he chose this letter. A reading of his paper indicates that it was an arbitrarily chosen symbol. This was apparently done like stating, "Let  $\chi$  represent ... ." For example, Gibbs used  $\eta$  for entropy, and Planck later used  $\Phi$ .  $S$  has become the standard symbol for entropy.

The term "energy" seems to be fairly universally used. However, the symbol  $U$  was apparently preferred in Europe (Clausius, e.g., used  $U$ ), and  $E$  in the United States. For some reason the word "energy" has not been deemed sufficient, and other descriptives such as "internal energy" and "total energy" are in common use for the first law energy. We prefer the unmodified term.

Two conveniently defined functions are those that were originally described by using the word "free" to indicate that under special conditions, these were energies that were "free" or available for work. In modern terms we use Gibbs energy or Gibbs function and Helmholtz energy or

\*Corresponding author.

Helmholtz function; the descriptive “free” has been banished although it unfortunately continues to be used. The Gibbs and Helmholtz energies are useful functions of convenience and are not fundamental in the same sense as the energy and the entropy. In modern terms  $G = H - TS$  and  $A = E - TS$ , and changes in both *must* be determined along *reversible* paths. Although irreversible or spontaneous changes of state may occur, these functions are solely functions of the end states, and must be evaluated using reversible paths.

Gibbs used the symbol  $\zeta$  for the Gibbs function and  $\psi$  for the Helmholtz function. Planck used  $F$  for the Helmholtz function (from the freie Energie named by Helmholtz), but didn't directly define a Gibbs function. His  $\psi = S - H/T$ , and in modern terms this would be  $\psi = -G/T$ . Epstein used  $F$  for the Gibbs function and  $\psi$  for the Helmholtz function. Lewis used  $F$  for the Gibbs function and  $A$  for the Helmholtz function. For many years the symbol  $F$  was used in Europe for the Helmholtz function and in America for the Gibbs function. IUPAC finally resolved this by banishing  $F$  completely. Caution must be used in reading the older literature.

In the hope of making this history clearer we present in Table 1 for each function and effect a tabulation of the symbols used and an indication of the probable origins or originator.

Gibbs defined  $\mu$  as “differential coefficients of  $\epsilon$  (energy) taken with respect to  $m_1$  and  $m_2 \dots$ .” This is now called the chemical potential. Epstein called it the “partial molal thermodynamic potential.” In modern notation  $\mu_i = (\partial G/\partial n_i)_{T,P,n_j}$ .

IUPAC defines a partial molar quantity  $X_B$  as  $(\partial X/\partial n_B)_{T,P,n_{j \neq B}}$ . The word “partial” comes from this being a partial derivative. Lewis (1907) defined a partial molecular volume. Gibbs wrote about a partial specific quantity. Lewis and Randall use partial molal. Guggenheim preferred to simply use “partial quantities,” and Keenan to use “partial properties.” Although partial *molal* is commonly used, we prefer IUPAC's usage of partial *molar* as being more accurate.

We trust that this brief history of some thermodynamic notation has been of interest.

### Literature Cited

1. Mills, I.; Cvitas, T.; Homann, K.; Kallay, N.; Kuchitsu, K. *Quantities, Units and Symbols in Physical Chemistry*; IUPAC; Blackwell Scientific: Oxford, 1988.
2. Carnot, S. *Reflections on the Motive Power of Fire*; E. Mendoza, Ed.; Dover: New York, 1960 (originally published in 1824).
3. Clausius, R. *Ann. Phys. Chem.* **1865**, *125*, 368.

Table 1. Origin of Symbols Used for Thermodynamic Functions

Name	Etymology	Symbol	Source
Pressure	pressura (L)	$P$	
Volume	volumen (L)	$V$	
Temperature	temperatura (L)	$T$	
	temperature (Fr)		
Work	work, werk, weorc (ME)	$W$	
	worc, werc, weorc (AS)		
Heat	hete, haete (ME)	$Q$	calorique (Fr)
	heiza, heiza (OHG)		Lavoisier ?
	Hitze (G), hitte (D)		
Energy	energia (LL)	$U$	
	energeia (Gr)	$E$	
	energie (Fr)		
Enthalpy	ενθαλπειν (Gr)	$H$	Clapeyron ?
			Clausius ?
		$\chi$	Gibbs
		$X$	Epstein
Entropy	η' τροπη' (Gr)	$S$	Clausius
		$\eta$	Gibbs
		$\Phi$	Planck
Gibbs energy		$G$	IUPAC
		$\zeta$	Gibbs
		$\Phi$	Epstein
		$F$	Lewis
		$\Psi$	Planck
			(= $-G/T$ )
Helmholtz energy	freie Energie	$A$	IUPAC
	(Helmholtz)	$F$	Planck
		$\psi$	Gibbs
		$\Psi$	Epstein
Chemical Potential		$\mu$	Gibbs