Thermodynamics of Nitinol

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A self-consistent macroscopic thermodynamics is developed for the calculation of work, heat, and dissipation for thermodynamic paths of the shape memory alloy, Nitinol. The thermodynamic system analyzed is a Nitinol helix for which extensive force-length-temperature (FLT) equation of state measurements have been made. The Nitinol system exhibits significant hysteresis and is determined to be a nonequilibrium thermostatic system. A set of equations of state are provided which correlate all reversible and irreversible Nitinol thermodynamic paths to both the set of helix (FLT) thermodynamic state variables and to new "history" state variables. It is shown that these equations predict observed cyclic behaviors not previously interpreted. In the absence of calorimetric measurements for the Nitinol helix system, a physical assumption is made that reversible paths are of constant phase. This assumption is used to estimate the reversible path thermal and mechanical heat capacities for the Nitinol system. With the state equations and the estimated reversible path heat capacities, the nonequilibrium thermostatic formalism is employed to derive expressions for the heat flow for any Nitinol thermodynamic path. It is shown that predicted calorimetric quantities are in good qualitative agreement with measurements. It is also shown that the calorimetric quantities are sensitive to state equation coefficients, which in turn are sensitive to cold-working or "conditioning" of the material. The large heat of transformation, \( \sim 2.4 \text{ cal/g} \), an estimated isentropic temperature change of 22 °C and the large dimensional changes associated with the shape memory effect, imply that Nitinol may be useful for many applications, including use as a working medium for low-grade thermal-energy conversion (i.e., heat engines).

I. INTRODUCTION

Shape memory alloys have the remarkable property of being easily deformed at low temperatures, but rapidly and forcefully recovering their "remembered" shape upon heating.\(^1\)\(^-\)\(^5\) The potential utility of this behavior has led to considerable attention in recent years, and work is progressing from the exploratory research stage toward practical applications.\(^1\)\(^-\)\(^7\) However, engineering design and development has been hampered by lack of a thermodynamic treatment which both accounts for the complex state behavior of shape memory alloys, including hysteresis, and permits accurate and predictive calculations of work, heat, and dissipation for all processes. It is the purpose of the present paper to provide an empirically based macroscopic thermodynamic description which will satisfy these requirements for the nickel-titanium alloy, Nitinol. The approach adopted for development of this thermodynamics is the nonequilibrium thermostatics.

Neither statistical mechanics nor traditional thermodynamics were found applicable to Nitinol. The statistical mechanics formalism is based on assumed knowledge of the microscopic physical processes which are responsible for observed behavior. Although Cohen and his collaborators,\(^8\)\(^-\)\(^11\) Mohamed,\(^12\) Wayman,\(^13\) Golestaneh,\(^14\) and others\(^2\)\(^-\)\(^5\) have identified a large number of physical mechanisms which may contribute to the complex behavior of shape memory alloys, no statistical mechanical development based on these mechanisms has resulted in an accurate thermodynamic prediction of the type of phenomena observed for these materials (see, e.g., Figs. 1 and 2).

The complex nature of Nitinol also poses a problem for application of traditional thermodynamic formalisms, although several such applications have been attempted.\(^15\)\(^-\)\(^19\) Fundamental assumptions of both equilibrium and relaxa-

![Figure 1](https://example.com/image1.png)

**FIG. 1.** Nitinol helix isotherms, axial force vs helix pitch (after Cory, Ref. 22).
II. REVIEW OF NONEQUILIBRIUM THERMOSTATICS (NET)

It has been shown\textsuperscript{20} that systems which exhibit hysteresis violate the assumptions of equilibrium thermodynamics. Since Nitinol is such a system, the nonequilibrium thermodynamics formalism\textsuperscript{20} developed for time independent hysteretic (thermostatic) systems will be applied herein to the Nitinol system. In this section nonequilibrium thermostatics (NET) is reviewed briefly.

The equations of state for NET systems are much more complicated than in simple equilibrium systems for which thermodynamic paths lie on a single two-dimensional (2D) state surface. Rather, the set of thermodynamic paths for systems with hysteresis fills a three-dimensional (3D) state volume. State paths within the state volume are "history" dependent. One assumption of NET is that a restricted set of reversible paths exist in the state space, and a new state variable, \( Z \), is defined such that paths of constant \( Z \) are reversible.

NET systems actually span a six-dimensional state space. A major assumption of NET is that three of these six variables can serve to completely quantify the history dependence of state paths. The three history variables comprise the coordinates of the last point along a system path at which \( dZ \) changed sign. Once the "history" variables are set (at the last state point at which \( dZ \) changed sign), all possible thermodynamic paths with \( dZ \) of the appropriate sign satisfy a state equation in the remaining 3D space. Therefore, these paths all lie on a single state surface, thus reducing the effective state space to 2D. However, there is an infinite set of such 2D state surfaces, one for each set of history variables.

All conventional equilibrium thermodynamics results which arise directly from the first law of thermodynamics,

\[
du = dq + dw,
\]

are also valid for NET.\textsuperscript{20} Here \( du \), \( dq \), and \( dw \) are the differential changes in internal energy, the path dependent heat into the system, and the path dependent work performed by the surroundings on the system, respectively.

By way of contrast, NET deductions from the second law differ greatly from equilibrium thermodynamics results. The differential form of the second law for NET systems is borrowed directly from nonequilibrium (relaxation) thermodynamics to include an internal entropy generation term\textsuperscript{20}.

\[
Tds = dq + Tds, \tag{2}
\]

where \( T \) is the absolute temperature, \( ds \) is the differential entropy change of the system, and \( ds \) is the internally generated entropy change for the differential path element. It has been proven\textsuperscript{20} that such a term is necessary and sufficient for systems which exhibit experimental irreversibility, i.e., hysteresis. The modified form of the second law results in a new state function, \( R \equiv Tds/sdZ \), which provides a direct measure of internal energy dissipation along any NET system path. The NET formalism is applied to Nitinol in the following section.

III. NITINOL EXPERIMENTAL DATA

The Nitinol data necessary to complete the NET analy-
sis can be divided into three portions: (a) qualitative measurements to assure that the Nitinol system is a NET system, (b) mechanical force-length-temperature (FLT) measurements sufficient to ascertain the state equations and the $Z$ equation (reversible) relationships satisfied by the system, and (c) calorimetric measurements sufficient to determine the Nitinol system heat capacities.

The Nitinol system considered here comprises a Nitinol helix for which extensive mechanical FLT data have been taken.\textsuperscript{22,23}

### A. Qualitative measurements

The work variables selected for the helix measurements were the externally applied axial force $F$ required to extend the helix, and the specific length $L$, which for the case of the helix, is the axial length per unit mass.

Qualitative measurements\textsuperscript{22,23} showed that the Nitinol helix is a NET system\textsuperscript{20}; hysteresis was observed (e.g., see Figs. 1 and 3); the system was shown to be a time and rate independent nonrelaxation type system; reversible path elements, albeit limited, were identified; and experimental techniques were found which provided reproducible measurements. (The major impediment to reproducible measurements was cold working, or "conditioning." The action of making the measurements can alter the physical properties.\textsuperscript{22-26} Therefore, it was found necessary to stabilize the material by thermomechanical cycling\textsuperscript{22,23} until the act of measurement no longer changed the physical properties of the system.)

### B. Nitinol state behavior

The raw mechanical FLT measurement data sufficient to determine the state and $Z$ equations are provided in the supplementary report to Ref. 22. The correlation of these data into state and $Z$ equations has been reported.\textsuperscript{22,23}

A schematic diagram illustrating the Nitinol (helical element) behavior in FLT state space is provided in Fig. 3. Figure 3 is incomplete at large length and large force because of experimental difficulties in obtaining reproducible data in these regions.

Experimental measurements established that all possible Nitinol thermodynamic paths lie within the FLT volume bounded by the Austenite $\rightarrow$ Martensite (AM) and Martensite $\rightarrow$ Austenite (MA) boundary surfaces. Further, the measurements showed that the AM and the MA boundary surfaces are asymptotic surfaces, i.e., any thermodynamic path for which the Austenite to Martensite transformation occurs will approach asymptotically the AM boundary surface. Analogously, any thermodynamic path for which the Martensite to Austenite transition occurs will approach asymptotically the MA boundary surface. The nature of the behavior between the boundary surfaces is illustrated in Fig. 1.

One of the important behaviors not illustrated in Figs. 1 and 3 concerns reversible paths. Experimentally it was found\textsuperscript{22,23} that there is a restricted set of thermodynamic paths for which Nitinol behaves reversibly and can be cycled without the appearance of hysteresis. The observation of reversible paths, coupled with measurements of the boundary surfaces and the specific behavior between the boundary surfaces, was used to formulate analytic equations of state for Nitinol.

### 1. Nitinol analytic equations of state

Two assumptions were made to aid in formulating the Nitinol equations of state. First, the region of interest was assumed to reside in the helix state space region for which the AM and MA boundary surfaces (Fig. 3) are well approximated by parallel plane surfaces. Secondly, these planes were then assumed to extend without limit in the FLT space; i.e., both the elastic behavior at low force and at high force, and the behaviors which occur at very high force (e.g.,...
yield and failure) were ignored for the present approximation. The equations for the AM boundary surface \( (B_{AM}) \) and MA \( (B_{MA}) \) are

\[
F_g(L,T) = F_{BAM}(L,T) = (a - f)L + (b + g)T - N, \tag{3}
\]

\[
F_{BMA}(L,T) = F_B(L,T) - h. \tag{4}
\]

The constant coefficient \((a - f)\) is obtained by measurement of \(dF_B/dL\) at constant temperature, while the coefficient \((b + g)\) is determined by measurement of \(dF_B/dT\) at constant length. \(N\) is determined by evaluating Eq. (3) at any FLT coordinate point on the top boundary surface in the state space region of interest. The coefficient \(h\) is the force separation (size of hysteresis) of the boundary surfaces at constant temperature and constant length (see Fig. 4). A state variable \(Z\) was defined to characterize the observed set of reversible Nitinol thermodynamic paths. The relationship \(Z = Z(F,L,T)\) defines mathematical reversible surfaces in the state space, i.e., surfaces of constant \(Z\). The intersection of these mathematical reversible surfaces with the real Nitinol state surfaces provides the restricted set of reversible Nitinol thermodynamic paths. For the Nitinol helix system, measurements indicated \(^{22,23}\) that the \(Z\) surfaces are well approximated by parallel plane surfaces:

\[
Z = aL + bT - F. \tag{5}
\]

The coefficients \(a\) and \(b\) were determined by measurement of \(dF/dL\) at constant \(Z\) and \(T\), and \(dF/dT\) at constant \(Z\) and \(F\). \(^{23}\)

Most possible thermodynamic paths lie between and not on, the AM and MA boundary surfaces of Fig. 3. The FLT state data for AM paths were found to be well approximated by the relationship

\[
\frac{F_B - F}{F_{BS} - F_x} = \text{exp}\left(\frac{g(T - T_x) - f(L - L_x)}{F_{BS} - F_x}\right) \tag{6}
\]

and for the MA paths,

\[
\frac{F - (F_B - h)}{F_0 - (F_{BS} - h)} = \text{exp}\left(\frac{g(T_0 - T) - f(L_0 - L)}{F_0 - (F_{BS} - h)}\right), \tag{7}
\]

where (see Fig. 4), the subscript \(x\) is used to denote the “history” variables and indicates the state point \((L_x, T_x, F_x)\) at minimum \(Z = Z_x\) \((F_x, L_x, T_x)\), i.e., last reversal in sign of \(dZ\) from \(<0\) to \(>0\), for the AM surface in question. Similarly, the subscript \(0\) labels the state point \((L_0, T_0, F_0)\) of maximum \(Z = Z_0\) \((F_0, L_0, T_0)\) for the MA surface considered. Also, \(F_{BS} = F_B(L_x, T_x)\) and \(F_{BS} = F_B(L_0, T_0)\). The parameters \(a, b, f, g, h,\) and \(N\) are constants for the Nitinol helix equations of state, and the measured values for the conditioned helix (and for wire) \(^{24,27}\) are provided in Table I.

Equations (6) and (7) each have six independent variables: the mechanical behavior variables \(F, L,\) and \(T,\) and the “history” variables \(F_x, L_x,\) and \(T_x\) (or \(F_0, L_0,\) and \(T_0\)). These six variables form a six-dimensional space completely describing the state behavior of Nitinol.

Note: These variables are the most useful for experimental work, but an alternate set of variables, \(P, Z, T, P_x, Z_x, T_x,\) has been found mathematically more convenient and does a better job of displaying many of the properties of the state equations. The transformations to the new variables uses Eq. 5 to define \(Z, T = T,\) and we define a force coordinate (see Fig. 4)

\[
P(L,T) = F_B(L,T) - F(L,T). \tag{8}
\]

The state equations (6) and (7) can be expressed in terms of \(P\) and \(Z\) by using Eqs. (5) and (8) as coordinate transformations. Any AM surface can be expressed as

\[
Z - Z_x = P - P_x - P_x \ln(P/P_x); \tag{9}
\]

and similarly, any MA surface can be represented in the form

\[
Z_0 - Z = P_0 - (h - P_0) \ln[(h - P)/(h - P_0)]; \tag{10}
\]

Each of these (mathematically) simpler forms is independent of temperature and involves only four variables.

C. Calorimetric measurements

Two types of calorimetric data have been reported for Nitinol; thermal heat capacity and the heat of transformation, both measured at constant force. Furthermore, except for Mercier and Melton, \(^{28}\) data have been taken only for the zero applied force case. No measurements of specific heat at constant length (strain) are known to the authors. The forms of the Nitinol samples were wire, rods, or disks. In none of these cases were the samples conditioned (stabilized). The Nitinol samples also varied considerably in composition among the reported investigations. However, the following observations or trends were common among the measurements \(^{26,37}\):

(a) The specific heat along a constant force path, when measured as a function of temperature, shows a sharp peak in the Martensite-Austenite transition temperature range both for heating and for cooling paths. \(^{28,37}\) The specific heat peak during heating occurs at a higher temperature than the peak observed when cooling (see Fig. 2).

(b) Thermal cycling of a Nitinol sample resulted in reduced height of the constant force specific heat peaks. \(^{31}\)

That is, the specific heat at constant force is a function of the sample conditioning; just as FLT behavior is a function of conditioning. \(^{22,24}\)

(c) The heat of transformation, deduced from the \(C_F\) measurements, ranged from 1.26 cal/g to values as high as 9.3 cal/g. \(^{28,37}\) With thermal cycling (conditioning) the heat of transformation was observed to decrease. \(^{31}\)
Unfortunately, no calorimetric measurements have been performed on the conditioned Nitinol (helix) sample for which detailed state surface measurements were made. Furthermore, no state equation measurements have been reported for Nitinol samples for which calorimetric measurements have been published. Therefore, there is no Nitinol system known to the authors at this date for which a sufficiently complete set of data have been taken to complete an empirically based thermodynamic description.

IV. ASSUMPTIONS FOR MISSING DATA

In this section plausible assumptions will be employed to estimate quantitatively the calorimetric data needed to complete the NET description for the Nitinol helix system. Specifically, two quantities will be sought: the thermal heat capacity on reversible paths

$$C_z \equiv \left( \frac{d'q}{dT} \right)_z ,$$  

(11)

and the mechanical heat capacity

$$\theta_z \equiv \left( \frac{d'q}{dZ} \right)_r .$$  

(12)

These can be transformed to other heat capacities via Eqs. (27) of Ref. 20.

A. Thermal specific heat for reversible paths, $C_z$

The first assumption made is that no phase transformation occurs along any path on a reversible surface. Although the only real (observable) paths on the reversible surface are those formed by the intersection of the state surface with the reversible surface, one can treat the thermodynamics on the entire (mathematical) reversible surface using reversible equilibrium thermodynamics. Then, the state equation, $F = aL + bT - Z$, and one calorimetric quantity specified everywhere on the reversible surface are the only data required. If no phase transformation occurs anywhere on any constant $Z$ surface, and if it is assumed that the temperature region of interest lies well above the lattice Debye temperature, then the specific heat at constant specific length on the reversible surface, $C_{LZ}$, should be well approximated as a constant. (Specifically, the Petit–DuLong approximation for equal atomic percentages of Ni and Ti is used, so that $C_{LZ} = 468$ J/kg K.) With these assumptions the reversible thermodynamics on the reversible surface is straightforward.\(^{38}\)

Since reversible thermodynamics is assumed to describe all paths on the reversible surface, it must describe the particular path which is the intersection of the reversible surface with the state surface, i.e., a constant $Z$ path on the state surface. From the reversible (equilibrium) thermodynamics the heat capacity on such a path can be shown by straightforward analysis\(^{39}\) to be

$$C_z = \left( \frac{d'q}{dT} \right)_z = C_{LZ} - \frac{b g}{f} T ,$$  

(13)

where $b$, $g$, and $f$ are the measured Nitinol state equation parameters described in Sec. III above. Note that this form for $C_z$ is a function of temperature only, and does not depend on any of the other state space variables.

B. The mechanical heat capacity $\theta_z$

To obtain $\theta_z$ it will first be necessary to obtain the dissipation state function $R$. Several constraints on $R$ have been identified. A fundamental constraint arises from the relationship\(^{30}\)

$$R \, dZ = Td_s > 0 .$$  

(14)

A second constraint is implicit in the mechanical behavior described by the state equations (see stable matched pairs, Sec. V). For isothermal, closed, stable cycle [Eq. (43), Ref. 20],

$$\oint R \, dZ = \oint Td_s = \oint f \, dL ,$$  

(15)

or in terms of the stated parameters, using the state equations,\(^{30}\)

$$\oint R \, dZ = (h \Delta Z - \Delta P^2)/f ,$$  

(16)

where $\Delta Z$ and $\Delta P$ are the magnitudes of the differences between extreme values for $Z$ and for $P$ for the isothermal closed, stable cycle.

Next, two assumptions will be made. Note that the derivatives with respect to temperature of $\oint R \, dZ$ in Eq. (16) vanish. The first plausible assumption is

$$\left( \frac{\partial R}{\partial T} \right)_Z = 0 .$$  

(17)

Since $R = R(Z,T)$, Eq. (17) implies that $R$ on any state surface is a function of $Z$ alone (in the $Z - T$ thermostatatic coordinates) without dependence on temperature, and the internal entropy generated depends only on the change in $Z$, and not on the specific path followed.

The second plausible assumption is that the symmetry between the stable matched AM and MA surface pairs (see Sec. V below) is such that the dissipation term in Eq. (16) is divided equally between the AM and the MA state isothermal paths.

Finally, it can be noted that as $\Delta Z$ is increased to very large values, $\Delta P$ is limited to $h$ (Fig. 4), i.e.,

$$\lim_{\Delta Z \to \infty} R = h / 2f .$$  

(18)

The requirements on $R$, Eqs. (14) and (16), the plausible assumption Eq. (17), the symmetry assumption, and the limit value Eq. (18) are not sufficient to determine uniquely $R(Z)$. However, they are highly restrictive. One final assumption will completely specify $R$; namely, $R$ varies exponentially with $Z$. With this assumption, $R$ takes the explicit form

$$R = h / 2f \{ 1 - A \exp \left[ - (Z - Z_s)/h \right] \}$$  

(19)

AM surface $(Z > Z_s)$ ,

$$= - h / 2f \{ 1 - A \exp \left[ (Z - Z_o)/h \right] \}$$  

(20)

MA surface $(Z < Z_o)$ ,

with

$$A = \frac{(\Delta P/h)^2}{1 - \exp \left[ - \Delta Z/h \right]} .$$  

(21)

This form for $R$ on the AM surface and on the MA surface satisfies all fundamental and experimental con-
Specific Length, L

FIG. 5. Lack of uniqueness of FLT state space, illustrated by three AM surface isotherms which pass through a single FLT state point. Note that each isotherm represents a different AM state surface. (Different "history" variables, $P_z$, $Z_z$.)

strains thus far identified for $R$.

With no additional assumptions, the mechanical heat capacity $\theta_z$ can be obtained from the nonequilibrium thermostatic equations [Eq. (42) of Ref. 20],

$$\theta_z = \gamma T - R,$$

where

$$\gamma = \left( \frac{\partial L}{\partial T} \right)_f \left( \frac{\partial F}{\partial Z} \right)_T,$$

(the Nitinol state derivatives are provided in Sec. V below). Equations (13) and (22) provide the two heat capacities sought in this section to complete the NET description of the Nitinol helix system.

V. PREDICTIONS AND APPLICATIONS

Two categories of results and predictions are produced by the present formulation; (A) thermodynamic path behavior, as described by the Nitinol state equations, and (B) heat, dissipation, and thermodynamic functions on these paths. (Space limitations preclude presentation of complete mathematical descriptions of methods or results. However, a more complete version is available.)

A. State equations and Nitinol thermodynamic path behavior

The path behavior predicted by Equations (5)–(7) or Eqs. (5), (9), (10), describes several unusual properties of Nitinol which are critical in calculating heat flows. These properties can be deduced directly from the equations.

1. Uniqueness

Uniqueness of state functions (e.g., $s$, $u$, $R$, etc.) is crucial for thermodynamics. Nitinol is not unique in FLT space, in the sense that knowledge of the FLT point is not sufficient to determine subsequent thermodynamic path behavior. A single point in the state space can have an infinite set of AM and of MA state surfaces which pass through that point. This lack of uniqueness is illustrated schematically in Fig. 5. This "history dependent" behavior is common among systems which exhibit hysteresis.

The path from the FLT point in question depends not only on the FLT point coordinates, but also upon the path to the point. However, each state surface for Nitinol is specified uniquely by the history coordinates $F_0$, $L_0$, $T_0$, i.e., the values of $F$, $L$, and $T$ at which the last change in sign of $dZ$ occurred.

Therefore, all Nitinol state points are unique, but in the six-dimensional $F$, $L$, $T$, $F_z$, $L_z$, $T_z$ space, rather than the three-dimensional FLT space. The state behavior for any state surface, characterized by fixed values of $F_z$, $L_z$, $T_z$, is completely unique in FLT space. [Notation: history variables frequently will be suppressed when the particular surface is evident, e.g., $U(F,L)$ is used to indicate $U(F, L, F_0, L_0, T_0).$]

2. Stable matched pairs of state surfaces

All closed cyclic paths must traverse at least one AM ($dz > 0$) and one MA ($dz < 0$) state surface. But most cycles cannot be repeated. A stable cycle is defined herein as one which can be retraced exactly an indefinite number of times. The state equations predict that stable cycles are possible only on "matched pairs" of state surfaces which satisfy two criteria: First, the AM and MA components of the matched pair must intersect twice; second, the lines of intersection, labeled $Z_x$ and $Z_0$, must form the respective starting bound-

FIG. 6. Schematic diagram of tube formed by stable matched pair of state surfaces in force-length-temperature state space. Paths of constant $F$, $L$, or $T$ are shown on the top (AM) surface with a solid curve, and on the bottom (MA) surface via dashed curves.
Stable State Surfaces

Specific Length

a) Length Constrained

b) Force Constrained

FIG. 7. Schematic drift behavior of (a) length constrained or (b) force constrained isothermal cycles.

TABLE II. Nitinol partial derivatives (see footnotes a and b).

<table>
<thead>
<tr>
<th>Derivative</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>(∂F/∂Z)_T</td>
<td>-1 + a/(fV)</td>
</tr>
<tr>
<td>(∂F/∂T)_L</td>
<td>(ag + bf)/f</td>
</tr>
<tr>
<td>(∂L/∂Z)_T</td>
<td>1/(fV)</td>
</tr>
<tr>
<td>(∂L/∂T)_L</td>
<td>g/f</td>
</tr>
<tr>
<td>(∂L/∂T)_F</td>
<td>-[(b + gV)/(a - fV)]</td>
</tr>
<tr>
<td>(∂Z/∂T)_L</td>
<td>-gV</td>
</tr>
<tr>
<td>(∂Z/∂T)_F</td>
<td>-[(ag + bf)/V]/(a - fV)</td>
</tr>
<tr>
<td>(∂F/∂L)_Z</td>
<td>(ag + bf)/g</td>
</tr>
<tr>
<td>(∂F/∂L)_T</td>
<td>a - fV</td>
</tr>
<tr>
<td>(∂F/∂Z)_L</td>
<td>-<a href="gV">(b + gV)/V</a></td>
</tr>
<tr>
<td>(∂L/∂Z)_F</td>
<td>h + gV</td>
</tr>
<tr>
<td>(∂L/∂Z)_T</td>
<td>-[(b + gV)/V]/[(ag + bf)/V]</td>
</tr>
<tr>
<td>(\gamma = (\partial L/\partial T)<em>{T_1} \partial F/\partial Z)</em>{T_1} )</td>
<td></td>
</tr>
</tbody>
</table>

a Note \( V \equiv 1 - P/P_x \) for AM surfaces, \( \equiv 1 - (h - P)/(h - P_o) \) for MA surfaces.
b \( a, b, f, g, \) and \( h \) are empirical coefficients (e.g., see Table I).

\[ \Delta P \equiv P_x - P_0 = 2P_x - h, \]
\[ \Delta Z \equiv Z_0 - Z_x = -\Delta P - P_x \ln[(h - P_x)/P_x], \] (24)
where \( \Delta Z \) and \( \Delta P \) are the magnitudes of the total \( Z \) and \( P \) excursions for the matched pair of surfaces. The matched state surface pair forms a tube in FLT space, with extremities at \( Z_x \) and \( Z_0 = Z_x + \Delta Z \), as indicated in Fig. 6.

3. Cyclic drift

Since the stable pair of state surfaces is so explicit one may ask how, in an experimental device, such specific conditions can be obtained. The answer is that the Nitinol element will almost certainly not be on one of the stable surfaces initially, but, under repetitive cycling, the element will drift rapidly (a few cycles under most conditions) onto a stable state surface pair. This behavior is predicted by the state equations, has been confirmed experimentally, and has been observed in Nitinol heat engines as a startup performance transient. Isothermal cyclic drift between two fixed lengths, or between two fixed forces, is illustrated schematically in Fig. 7(a) or 7(b), respectively.

4. State equation partial derivatives

A number of partial derivatives which are frequently required in thermal calculations arise directly from the state equations. A set of such derivatives for Nitinol AM and MA state surfaces is listed in Table II. [These results are expressed in terms of \( P \), but can be transformed to FLT via Eq. (8)].

5. Hysteresis loss

A measure of the internal losses for a cycle of any type (constant force, etc.) on a stable matched pair of state surfaces, can be obtained from the isothermal hysteresis integral \( \oint \Phi F dL \) of an isothermal cycle between the same \( Z_x \) and \( Z_0 \), because \( R(z) \) is a state function. Here the operator \( \oint \) is defined as a stable (repeatable) closed, isothermal cyclic integral.

The cyclic integral can be evaluated in a straightforward...
way using the state equations (6) and (7). Expressing the result in terms of the cyclic \( Z \) and \( P \) excursions, one obtains
\[
\oint F \, dL = \frac{(h \Delta Z - \Delta P^2)}{f}.
\]

B. Heat and dissipation

A central objective of the Nitinol thermodynamics developed herein is to provide experimentally verifiable quantitative predictions of the heat flow into a Nitinol system for any specified thermodynamic path. This section provides specific verifiable predictions for Nitinol with the measured mechanical properties given in Table I and the approximations outlined above. The general technique for making the predictions is outlined so that the quantitative predictions of the theory can be extended to shape memory alloys with properties different from those given in Table I.

1. Heat flows

In \( Z, T \) thermodynamic coordinates on any particular state surface, the heat flow into a Nitinol system can be written in the form
\[
\Delta q = C_z \, dT + \theta_z \, dZ,
\]
where \( C_z \) and \( \theta_z \) are the thermal and mechanical heat capacities. For Nitinol, approximate forms are given by Eqs. (13) and (22), respectively, as developed in Sec. IV.

Equation (26) can be transformed to other thermodynamic coordinates (e.g., \( L, T, F, T, \) etc.) via Eqs. (27) provided in Ref. 20.

For example, in \( L, T \) coordinates
\[
\Delta q = C_L \, dT + \theta_L \, dL,
\]
with
\[
C_L = C_z - \theta_z \left( \frac{\partial Z}{\partial T} \right)_L \left( \frac{\partial Z}{\partial L} \right)_T
\]
\[
\theta_L = \theta_z \left( \frac{\partial Z}{\partial L} \right)_T
\]
and the partial derivatives of \( Z \) are provided in Table II. Heat flows for any Nitinol thermodynamic path can be computed from a path integral of Eq. (26) [or its transformed equivalents, e.g., Eq. (27)] provided in Ref. 20.

2. Thermodynamic state functions

The thermodynamic functions, i.e., internal energy \( u \), entropy \( s \), etc. are uniquely defined on each state surface. Both the system internal energy and the system entropy can be determined within a constant by straightforward path integrals; combining the first law, \( du = dq + F dL \), with Eq. (26), and the partial derivatives of \( L \) (given in Table II),
\[
\Delta u = \left[ C_z + F \left( \frac{\partial L}{\partial T} \right)_Z \right] \Delta T + \left[ \theta_z + F \left( \frac{\partial L}{\partial Z} \right)_T \right] \Delta Z,
\]
\[
u(Z,T) = u(Z,T) + F(T, T) + \int_{T_1}^{T} \left[ C_z + F \left( \frac{\partial L}{\partial T} \right)_Z \right] \Delta T
\]
\[
+ \int_{Z_1}^{Z} \left[ \theta_z + F \left( \frac{\partial L}{\partial Z} \right)_T \right] \Delta Z.
\]
3. Heat capacities

Thermal heat capacities can be calculated from Eq. (26) via appropriate thermodynamic coordinate transformations:

\[
C_F = \frac{d'q}{dT}_F = C_z + \theta_z \left( \frac{\partial z}{\partial T} \right)_F, \quad (32)
\]

\[
C_L = \frac{d'q}{dT}_L = C_z + \theta_z \left( \frac{\partial z}{\partial T} \right)_L. \quad (33)
\]

Then

\[
C_F - C_L = \theta_z \left[ \left( \frac{\partial z}{\partial T} \right)_F - \left( \frac{\partial z}{\partial T} \right)_L \right]. \quad (34)
\]

Figures 8–11 show the predicted heat capacities as a function of temperature for the Nitinol systems specified in Table I. These quantitative predictions can be proved or disproved by differential thermal analysis (DTA) measurements for which the temperature is cycled between 300 and 420 K, to provide 100% phase conversion (Figs. 8–10), and partial transitions (Fig. 11).

Figure 8 shows the predicted \( C_F \) for zero force heating and cooling paths for the Nitinol helix. Figure 9 shows the predicted \( C_F \) for the Johnson wire (dashed curves) and the effect on the predictions of increasing the parameters \( f \) and \( h \), respectively, to 30.0 N kg/m and 117 N (dotted curve) from the values given in Table I. The difference, \( C_F - C_L \) for the helix is plotted in Fig. 10.

Figure 11 shows the predicted DTA results for the Johnson wire for partial phase conversion cycles. The DTA experimental procedure would consist of heating the sample to about 400 K, then measuring \( C_F \) at zero force as the temperature is reduced to 329 K, and then increasing the temperature to 400 K. The predicted results are curves 1 (dashed lines). Next, to produce curve 2 (dot-dashed lines), the temperature is reduced to 340 K, and then increased back to 400 K. Note the discontinuous drops in \( C_F \) are predicted to occur at the reversal temperature of 340 K, and at 378 K. The latter is a decrease of 2 K from the full cycle prediction. Finally, to produce curve 3, the temperature is decreased to 359 K. As the temperature direction is then reversed there is a discontinuity in \( C_F \). Then the temperature is again increased back to 400 K. For this partial conversion cycle, the heating peak of \( C_F \) is predicted at 373 K.

The predictions of the NET theory show many features not available from conventional equilibrium or relaxation thermodynamics. \( C_F \) is strongly temperature dependent, with the heating and cooling peaks displaced in temperature. \( C_F \) is discontinuous (peaks) at a value which depends on the extent of the temperature cycle. \( C_F \) is significantly different from \( C_L \), therefore use of a generalized heat capacity in applications, e.g. heat engine efficiency calculations, will result in both qualitative and quantitative errors. Finally, the heat capacities are strongly dependent on the Nitinol state parameters, as exemplified in Fig. 9. This implies that heat capacity measurements cannot be compared directly, unless the results are rationalized by also measuring the state equation parameters.

The limited heat capacity data available in the literature seem to validate the predictions of NET. The results of Mercier and Melton are plotted on Fig. 9 (the boxes are data points taken from their graph). Even though the state parameters \( (a, b, f, g, h, N) \) for their 3-mm disks were not available, the data are fitted very well by a reasonable change in the Johnson wire parameters as listed in Table I. Conditioning, such as done by Johnson, has been shown to decrease \( f \) and \( h \). The changes in \( f \) and \( h \) required to fit the data were about as would be expected for a less conditioned sample. Furthermore, a decrease in the height of the \( C_F \) peaks has been observed as a consequence of repeated thermal cycling (i.e., conditioning).

The excellent agreement between NET predictions and the Mercier and Melton data in almost all features of the complex \( C_F (T) \) is a strong argument for the validity of NET. The only disagreement concerns the predicted discontinuous change in \( C_F \) at 100% phase conversion. While the disagreement may be caused by experimental limitations (discontinuous changes are notoriously difficult to measure), there is good reason to believe the state equations are inadequate in this region.

State surface measurement of the parameters \( a, b, f, g, N \) near the 100% conversion boundaries show considerable curvature as the shape memory boundary surfaces coalesce.
continuously into, and join the elastic boundary surfaces. Clearly the NET approximation of plane, flat boundary surfaces [Eqs. (3) and (4)] are inadequate in this region. A validation that this is the source of the theory–experiment disagreement is suggested in the experiment shown in Fig. 11. For this temperature cycle measurement, a discontinuous change in $C_p$ is predicted in path 2, at 340 K and in path 3 at 359 K where the temperature is experimentally reversed prior to achieving 100% conversion. This discontinuity prediction is independent of the theory approximations near the 100% conversion regions.

4. Latent heat

The latent heat $l$ is conventionally defined as the heat per unit mass absorbed (emitted) during an isothermal change in phase. For Nitinol the latent heat would be experimentally measured by isothermally straining the sample, and can be computed from Eq. (26) by integrating $\theta$ with respect to $Z$ over the $Z$ range (or $\theta_L$ over the $L$ range) for the phase transformation from Martensite to Austenite along an isothermal path,

$$l = \int \theta dZ.$$  \hfill (35)

Using Eqs. (18)-(25) and Table II, this results in

$$l = T \left[ \frac{b + g}{f} (\Delta L)_T (g \Delta P/f) \right] - \left[ \frac{1}{2f} \left( h \Delta Z - \Delta P \right) \right],$$  \hfill (36)

where in this equation $\Delta$ denotes 100% phase transformation.

Expressed in terms of the isothermal specific length difference between the Martensite and Austenite elastic boundaries, $(\Delta L)_T$,

$$l = T \left[ \frac{b + g}{f} (\Delta L)_T (g \Delta P/f) \right] - \frac{1}{2f} \left( h \Delta Z - \Delta P \right),$$  \hfill (37)

where $(\Delta L)_T$ is obtained in terms of $\Delta P$ (or $\Delta Z$) via integration over $Z$ of $(\partial L / \partial Z)_T$ from Table II:

$$(\Delta L)_T = \frac{1}{f} (\Delta Z + \Delta P).$$  \hfill (38)

The quantities $\Delta Z$, $\Delta P$, and $(\Delta L)_T$ are each positive as used in Eqs. (36)-(38).

The second term in Eq. (36) represents dissipation and, in general, is quite small compared with the temperature-dependent term; about 1% for the Nitinol helix.

Unfortunately, neither $\Delta Z$ nor $(\Delta L)_T$ has been measured for the Nitinol system for which state surfaces or calorimetric measurements have been made. However, $(\Delta L)_T$ can be estimated. Helix specific length extends $\Delta L$ is related approximately to the Nitinol wire surface torsional strain extent $\Delta \epsilon$ by

$$\Delta L = (R_T / \rho \pi^2 \rho) \Delta \epsilon = 4400 \Delta \epsilon \text{ m/kg},$$  \hfill (39)

where the Nitinol helix radius $R_T$ and wire radius $\rho$ were taken from Table I, and a Nitinol density $\rho$ of 6340 kg/m$^3$ was used.

Estimating the isothermal strain difference between the Martensite and the Austenite elastic phases as $\sim 6\%$ at 300 K,$^{43}$ one obtains via Eq. (39) $(\Delta L)_T = 264 \text{ m/kg}$. For the Nitinol helix, using Eqs. (9) and (38), this implies $\Delta Z \approx 15N, \Delta P \approx h$ (agrees with observation). Then Eq. (37) yields

$$l = 9.2 \times 10^3 \text{ j/kg} = 2.2 \text{ cal/g}.$$  \hfill (40)

No experimental measurement of latent heat was found for comparison with the prediction. The corresponding entropy change for the isothermal phase change is $\Delta s = 32 \text{ J/kg K} = 7.7 \times 10^{-3} \text{ cal/g K}$.

5. Heat of transformation at constant force

A second measurement of the heat associated with phase transformation is the constant force heat of transformation. For first-order phase transformations isotherms are simultaneously isobars and there is no difference between the isothermal latent heat and the constant force heat of transformation. In the case of Nitinol, however, the phase transformation is not first order and, as heat is added at constant force to cause a phase transformation, there is a change in temperature as well. The temperature difference (at zero force) between the Austenite start $(A_i)$ and Austenite finish $(A_f)$ temperatures, can be computed from the derivative, $(\partial T / \partial Z)_T$, given in Table II, using Eq. (14), and the large cycle approximation $\Delta P = h$, $\Delta T_f = A_f - A_i$

$$\Delta T_f = A_f - A_i = \int_{A_i}^{A_f} \left( \frac{dT}{dZ} \right)_T (dZ) = \frac{(a - f) \Delta Z + ah}{ag + bf}.$$  \hfill (41)

Using the helix state parameters from Table I, and the estimate of $\Delta Z = 15 \text{ N}$, this results in $(\Delta T)_f = 38 \text{ K}$ (see Figs. 8–10) which compares well with the experiments (Figs. 13 and 15 in Ref. 22). The value of $A_i$ depends on the force and is obtained from the experimental data. For the helix characterized by data in Table I, at zero force, $A_i = 290 \text{ K}$.

The constant force heat of transformation is usually defined empirically as the total heat absorbed during a phase transformation at constant force, less the sensible heat. For Nitinol, heat absorbed at constant phase is taken as $fC_p dT$, whereas the total heat absorbed is $\int fC_p dT$, with each line integral performed along the constant force path.$^{42}$ Then, the constant force heat of transformation is [Eq. (26)]

$$\Delta H_f = \int_{A_i}^{A_f} (C_f - C_{ref}) dT,$$

$$= \int_{Z_i}^{Z_f} \left( - \frac{ag + bf}{af} \right) (R - R) dZ.$$  \hfill (42)

Here the line integral is from the Austenite start temperature (at $Z_i$) to the Austenite finish temperature (at $Z_f$). In the second part of Eq. (42), the integrand can be expected to change by only 10–20% for different samples of Nitinol. Conditioning, however, has been shown to change the limits of integration by factors of 3 or more.$^{24}$ This change in $\Delta Z_f$ can be rationalized by recognizing that the internal stresses in conditioned Nitinol probably prevent 100% conversion of the sample to Austenite, even when the external force is reduced to zero.

For the helix with the parameters given in Table I at zero force, and an assumed $\Delta Z_f = 15 \text{ N}$, the heat of transformation has the value $\Delta H_f = 2.4 \text{ cal/g}$. The sensitivity of...
The integration limits in Eq. (42) may account for a significant portion of the range reported for experimental measurements from 1.26 to 9.3 cal/g. The available measurements of $\Delta H_p$ without the state information on the state parameters are insufficient to either confirm or contradict NET theory.

NET theory predicts that agreement between different experimental measurements of $\Delta H_p$ will never be achieved until the results are rationalized by specification of the state parameters which characterize the Nitinol sample measured. (Note: measurements of $b + g$ indicate it is a universal constant equal to $6 \times 10^6$ N/m$^2$ K, within experimental error, for Nitinol of all alloy compositions and degrees of conditioning.)

On the same sample of Nitinol, the NET theory predicts the constant force heat of transformation will be larger than the isothermal latent heat by 0.2 cal/g. This difference is subject to experimental measurement as a check of NET theory. The experiments must be done carefully, however, to insure that the change in the state parameters induced by the isothermal stretching required to measure latent heat is properly included in the calculations.

6. Dissipation energy

The dissipation energy can be measured directly only for closed isothermal, stable cycles where all of the cyclic work (hysteresis area) is dissipated as heat. In all other cycles and paths, the dissipated energy is mixed with isentropic energy changes. The NET theory provides a means for separating dissipation and isentropic energy changes on any path. However, the NET dissipation predictions can be validated only via measurements of closed, isothermal, stable cyclic hysteresis.

From Eqs. (18)-(21), with $\Delta P$ = $h$ and $\Delta Z$ = 15 N, the helix specific energy dissipated during the isothermal Martensite to Austenite transformation is 118 J/kg = 0.028 cal/g, or 1.3% of $l$. This may be compared with five percent measured by Salzbrenner and Cohen for the shape memory alloy Cu-14Al-2.5Ni. The interesting point here is that the dissipation term can be dropped in the calculation of $l$ and $(\Delta H)_p$ with small error. In general, the dissipation term can be neglected in all heat flow calculations except near adiabatic paths or at sufficiently low temperatures. Nonetheless, hysteresis must be included in the heat and work calculations to insure that calculations are performed over the correct thermodynamic paths. (Otherwise significant errors can occur whether or not the dissipation term is included.) Note that dissipation cannot be neglected when computing cyclic work, e.g., see Fig. 1. The Nitinol helix hysteresis cycle energy dissipation $\frac{\partial F}{\partial L}$, Eq. (25), is plotted against the cyclical, isothermal, torsional strain extent in Fig. 12.

7. Adiabats/isentropes

An experimental path measurement which can replace or complement calorimetric measurements is the determination of the adiabatic path. This path can be predicted by combining Eqs. (2), (14), and (26):

$$ds = \frac{R \, dZ}{T} = \frac{dg}{T} = \frac{C_z \, dT}{T} + \frac{\theta_z \, dZ}{T}.$$  \hspace{1cm} (43)

This equation can be integrated over an adiabatic path, i.e., $dq = 0$. Using Eqs. (13) and (22) to define $C_z$ and $\theta_z$, path relationships can be readily worked out.

Similarly, the isentropic ($ds = 0$) path relationships can be obtained via integration of Eq. (43) to give a transcendental equation in $P$ and $T$, where $T_s$ and $P_s$ are the history variables for the surface on which the path is traced:

$$\ln \left( \frac{T}{T_s} \right)^{C_z} \left( \frac{P}{P_s} \right)^{\frac{(b + g)/f}{P}} = \frac{g}{f} \left[ (P - P_s) + b(T - T_s) \right].$$  \hspace{1cm} (44)

Recognizing $P_s(b + g)/f$ as a portion of $\Delta H_p$ or $l$, the similarities and differences between Eq. (44) and the ideal gas equation,

$$\ln \left( \frac{T}{T_s} \right)^{C_z} \left( \frac{P}{P_s} \right)^{\frac{(b + g)/f}{P}} = \text{constant},$$

are apparent. [The pressure $P$ in the ideal gas equation is not to be confused with the Nitinol force variable $P$ in Eq. (44).]

For NET systems, adiabatic paths differ from the isentropic path by the term $f(R/T)(dZ)_q$. This term is generally very small. As shown above, it is about 1% of the latent heat. Consequently, the experimental adiabatic, as well as the isentropic path, is well approximated by Eq. (44).

The temperature change along an isentrope upon one (the AM) of a matched pair of state surfaces has been computed from the transcendental equation (44) and the results are illustrated in Fig. 13 for the Nitinol helix described in Table I. This figure shows the expected change in Nitinol temperature as the helix is stretched isentropically, as a function of the wire surface isentropic cyclic strain extent.

The total isentropic temperature change available is frequently employed for heat engine design as a material figure-of-merit. From Fig. 13, this number is $\approx 22$ °C, assuming $\Delta Z = 15$ N (see above) for 100% phase change. This value is much larger than the isentropic $\Delta T$ available for known thermoelectric, thermomagnetic, etc., solid materials, but is much smaller than is available for most liquid–gas phase transformations.
8. Cycle analysis

Nitinol has been suggested as a working medium for heat engines which convert low grade thermal energy into useful mechanical or electrical forms. Thermodynamic cycle analysis is necessary to select an optimum working cycle for any particular desired performance (e.g., minimum cost per unit produced energy, maximum efficiency, maximum power output, maximum power per unit mass, etc.). Cycle analysis is also used to specify machine dimensions and to determine heat flow requirements. Detailed Nitinol thermodynamic cycle analysis is beyond the scope of the present paper, but some results have been published elsewhere. The energetic phase transformation, $\Delta H_{\text{trans}}$, and dissipation energy of 1% of transformation energy versus isentropic strain (for the Nitinol helix), in qualitative agreement to that obtained (for other Nitinol systems). Even when insufficient thermal data (two heat capacities) are not available for a particular system, we have demonstrated that NET provides a formalism for using general physical knowledge to make a rational, self-consistent estimate of the required data (via $C_2$ and $R$ in this paper). Once these thermal data and the state equation coefficients are obtained, we have demonstrated how path integrals can predict, for all possible paths, heat flows, unique state function values, heat capacities, latent heats, heats of transformation, dissipated energy, and adiabatic and isentropic paths. The predictions are quantitative, giving not only the values, but also the functional dependence on the state variables.

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The specific calorimetric predictions given in Sec. V, for the Nitinol helix system, cannot be compared directly with reported calorimetric experimental data for other Nitinol systems. The numerical values are shown to depend strongly on the values of the state equation coefficients (Figs. 8 and 9) and these coefficients were not reported with the measured calorimetric data. However, the shape and values predicted (Fig. 9 for $C_F$, 2.4 vs 1.26–9.3 cal/g for $\Delta H_F$, and dissipation energy of 1% of transformation energy vs 5% for a different shape memory alloy) fall well within the range of reported data. Indeed, the inconsistencies among the reported data can be interpreted by the predicted strong sensitivity of calorimetric values to conditioning (Fig. 9). The effect of conditioning on experimental reproducibility in work and behavior measurements, is widely acknowledged. But, only a few reports (e.g., Salzbrenner and Cohen's comparison of multiple and single crystal Cu–14Al–2.5Ni behavior) give sufficient data to quantitatively estimate the degree of conditioning of the calorimetric samples measured. We strongly recommend that future calorimetric measurements be correlated with mechanical FLT measurements on the same sample.

The energetic phase transformation, $\Delta H_{\text{trans}}$, of Nitinol a
useful material for many applications. Furthermore, the large predicted isentropic $\Delta T$ of $-22$ $^\circ$C serves as an excellent figure-of-merit for Nitinol as a working material for thermal energy conversion, i.e., for heat engines.

The quantitative thermal behaviors predicted by the NET have not been tested. A definitive test of the theory requires experimental measurements on a completely characterized (state equation coefficients plus two heat capacities) system. We recommend either calorimetric measurements on the Nitinol helix, for which the state coefficients are known$^{15}$; or, measurement of the state coefficients for thermally measured systems.

Another area deserving study is the identification and characterization of the microscopic physical mechanisms which are responsible for the complex behavior of Nitinol. For example, Olson and Cohen$^{9,10}$ have concluded that hysteresis is associated with the nucleation, growth path, and kinetics of Martensite platelets. A clear picture of how microscopic crystalline mechanisms affect Nitinol physical properties should stimulate development of improved materials for specific applications. The explicit characterization of behavior and the rigorous thermodynamic relationships provided here should be of great assistance in such endeavors.

23J. S. Cory, in Ref. 6, pp. 7.1–7.18.
24A. D. Johnson, in Ref. 6, pp. 10.1–10.29.
25R. M. Banks (private communication).
27E. C. Cady (private communication), the wire state equation coefficients were obtained by fitting the state equations of Sec. III of the present paper to 30 mil Nitinol wire data published in Ref. 24.
30R. J. Wasilewski (private communication).
38J. L. McNichols (unpublished calculations).
40J. S. Cory (unpublished measurements).
41A. D. Johnson (private communication).
42Note that $C_p \Delta T$ is the amount of heat absorbed for a constant force temperature-change, $dT$, and, by assumption, no change in phase (i.e., no change in Z). Actually, the (sensible) heat subtracted by the experimentalists$^{29-37}$ is that obtained by connecting $C_p$ at $A_1$ to $C_p$ at $A_2$ with a straight line on the $C_p$ vs temperature data plot, and integrating the energy below the line from $A_1$ to $A_2$.
43For the wire samples, conditioning reduced the isothermal strain between phases to $-4\%$ (Ref. 24). However, the helix torsional data indicated a conditioned value closer to $6\%$ (Ref. 22).
45D. M. Goldstein (private communication). Plans have been made to perform constant force specific heat measurements on samples of the Nitinol helix (Table I) at the Naval Surface Weapons Center, Silver Springs, MD.