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Calculation of the Specific and Volumetric Enthalpies of Ge-Si Alloys

Vasilios Alexiades
R. P. Wichner

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CALCULATION OF THE SPECIFIC AND VOLUMETRIC ENTHALPIES OF Ge-Si ALLOYS

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CALCULATION OF THE SPECIFIC AND VOLUMETRIC ENTHALPIES OF Ge-Si ALLOYS

Vasilios Alexiades

ABSTRACT

A procedure is developed for the calculation of specific and volumetric enthalpies of Ge-Si alloys as an initial step in the evaluation of these materials for heat storage in solar dynamic power systems. The calculation is based on the thermodynamics of non-ideal solutions and the reported "regular" nature of liquid and solid Ge-Si solutions. With only minor modifications, all of the other thermodynamics properties of this alloy system may additionally be evaluated.

Use of Ge-Si alloys for heat storage purposes in solar receivers entails both negative and positive aspects. The negative aspects relate largely to the non-congruent nature of the phase change process which precludes isothermal heat delivery. However, on the positive side are high thermal conductance, low volume change on melting, and the availability of a range of heat delivery temperatures by modification of only the alloy composition.

1. INTRODUCTION

Solar dynamic power systems are generally designed to include a thermal storage material in the receiver which provides heat to the turbine fluid during the eclipse portion of the cycle by the release of the latent heat of fusion of a phase change material (PCM). Ideally, one would select a congruently melting material for this purpose, i.e., either a pure compound or a eutectic mixture, so that the freezing or melting process may take place with no compositional change required between liquid or solid phases. In such a case, the heat release would be isothermal, at least theoretically, which is most appropriate for the heating portion of a thermodynamic cycle. In practical systems, however, isothermal heat supply in such a manner can never be achieved because significant temperature gradients are required in order to drive heat into and out of the storage material.

In this report, an initial evaluation is performed of the possible use of the non-congruently melting Si-Ge alloys for use as heat storage material for solar receivers. In this system, heat delivery and acceptance is not isothermal but occurs instead over some temperature range between the liquidus and solidus temperatures. In addition, compositional change is required for the process; i.e., both Si and Ge must move from liquid to solid phases at all times during the phase change process. However, if an adequate amount of heat may be stored within an acceptable ΔT between the liquidus and solidus temperatures and the mass transfer between phases proves to be sufficiently rapid, then use of Si-Ge alloys as PCMs provide a number of potential advantages, such as: (1) high thermal conductance, (2) a variable temperature range simply by adjusting the composition, and (3) high heat storage capacity per unit volume for the Ge-rich alloys and high heat storage per unit mass for the Si-rich compositions.

This report provides a necessary first step in the evaluation of the use of non-congruently melting Si-Ge alloys as heat storage materials for solar receivers. A calculational procedure is described for determining the enthalpy change between two given temperatures for Si-Ge alloys of arbitrary composition. An important aspect of the calculation is the evaluation of the heats of solution of the liquid and solid phases which continually form and vary in composition with each temperature change. The method for determining the heats of solution, based on pure component properties and the shape of the phase diagram, is described in Sects. 2 through 5. In Sect. 6, the method is applied to the Ge-Si system using the reported "regular" nature of these liquid and solid solutions.

The procedure for determining the enthalpy change in Si-Ge alloys is developed in a general way so that adaptation to other binary solution systems may be readily accomplished. The adaptation requires only revision of the input for the properties of the pure components, information regarding the nature of the solution (ideal, regular or non-regular), and the shape of the phase diagram throughout the region of interest. Furthermore, though this development emphasizes determination of the enthalpy change per unit mass and volume, it is seen that the

procedure applies as well to other thermodynamic properties; e.g., free energy and the entropy.

1.1 Approach and Notation

The calculation of any of the thermodynamic properties of the Ge-Si alloy system entails similar steps, therefore a general procedure may be adopted in terms of a generic thermodynamic property w(x,T,P) which for a given concentration (mole fraction), x, temperature, T, and pressure, P, may represent any of the following:

g = Gibbs free energy,

h = enthalpy,

s = entropy,

v = volume, and

c_p = heat capacity.

Use of the small case denotes a property per mole of substance. We will use the corresponding capital to denote the extensive property.

All of the above properties are inter-related (see Appendix A) and hence any one may be the basis for an estimation method from which all the others may be calculated. We chose to set up the calculation in terms of the Gibbs free energy, g(x,T,P). In addition, at the outset a general binary alloy or solution is considered, consisting of pure components, A (the solvent) and B (the solute). In Sect. 6, A is specified as Ge and B as Si. As composition variable we use the mole fraction of the solute, B;

$$x = x_B = \frac{N_A}{N_A + N_B} ,$$

whence

$$1 - x = x_A = \frac{N_A}{N_A + N_B}$$

represents the mole fraction of solvent A, N_A and N_B being the numbers of moles of A and B.

We shall use the following, rather standard notation:

$w(x,T,P)$ = Value of w per mole of alloy $A_{1-x}B_x$ at T, P,

$w^o(x,T,P)$ = (Raoultian) reference state for the alloy, equal to the molar average of the pure constituents,

$\Delta w^{id}(x,T,P)$ = Ideal solution increment for w^o,

$\Delta w^{ex}(x,T,P)$ = Non-ideal or excess increment for w^o,

$w_i^o(T,P)$ = Reference value for pure i = A, B,

$\overline{w}_i(x,T,P)$ = Partial molar value with respect to constituent i.

In condensed systems of modest pressure variation, the pressure effect on thermodynamic variables is generally negligible and will ultimately be dropped. By definition from the above,

$$w = w^o + \Delta w^{id} + \Delta w^{ex} \quad .$$

In the following Sects. 2 through 5, we outline the calculational procedures for determining the generic thermodynamic property, w, for ideal, regular, and non-ideal solutions, using largely methods described by Lupis[1] and by Brebrick et. al.[2] The procedure is applied in Sect. 6 to both the liquid and solid phases of the Ge-Si system and combined in the two phase regime by use of the lever rule. Results are obtained for h(x,T) in terms of both (J/g) and (J/cm^3) by means of a Fortran program listed in Appendix B. The results for h(x,T) are presented in Table 2 and Figs. 2 through 5.

2. THERMODYNAMIC FUNCTIONS OF MIXING

Consider N_A moles of pure A and N_B moles of pure B at temperature T and pressure P. The thermodynamic property w has the value $w_A^o(T,P)$ per mole of component A and $w_B^o(T,P)$ per mole of component B. Therefore the value is assigned

$$W^o = N_A\, w_A^o + N_B\, w_B^o \tag{2.1}$$

as the (Raoultian) reference value or, per mole,

$$w^o = x_A\, w^o + x_B\, w_B^o\ . \tag{2.2}$$

After mixing and equilibration at the same T, P we have $N_A + N_B$ moles of solution with

$$W = N_A\, \overline{w}_A + N_B\, \overline{w}_B\ , \tag{2.3}$$

or, per mole,

$$w = x_A\, \overline{w}_A + x_B\, \overline{w}_B\ , \tag{2.4}$$

where $\overline{w}_i(x,T,P) = \left(\frac{\partial W}{\partial N_i}\right)_{N_{k\neq i},T,P}$ denotes the partial molar w of component i in solution of concentration x, temperature T, and pressure P.

The change in w upon mixing, per mole of solution is therefore

$$\Delta w^{mix} = w - w^o = x_A\, \Delta\overline{w}_A^{mix} + x_B\, \Delta\overline{w}_B^{mix}\ , \tag{2.5}$$

expressing the integral Δw in terms of the partial $\Delta\overline{w}_i$, where

$$\Delta\overline{w}_i^{mix}(x,T,P) = \overline{w}_i - w_i^o\ ,\ i = A,B\ . \tag{2.6}$$

From the definition of partial properties, one obtains

$$\Delta\overline{w}_A^{mix} = \Delta w^{mix} - x\left(\frac{\partial \Delta w^{mix}}{\partial x}\right)_{T,P}, \tag{2.7}$$

$$\Delta\bar{w}_B^{mix} = \Delta w^{mix} + (1 - x)\left(\frac{\partial \Delta w^{mix}}{\partial x}\right)_{T,P} , \tag{2.8}$$

expressing the partial properties in terms of the integral property.

Traditionally, the partial Gibbs free energies of mixing, also called relative chemical potentials, are expressed in the form

$$\Delta\bar{g}_A^{mix} = \Delta\bar{\mu}_A = RT \ln a_A \tag{2.9}$$

$$\Delta\bar{g}_B^{mix} = \Delta\bar{\mu}_B = RT \ln a_B \tag{2.10}$$

where a_i = activity of component i. Hence

$$\begin{aligned} \Delta g^{mix}(x,T,P) &= (1 - x)\ \Delta\bar{\mu}_A + x\ \Delta\bar{\mu}_B \\ &= RT[(1 - x) \ln a_A + x \ln a_B] . \end{aligned} \tag{2.11}$$

The activities are, of course, functions of (x,T,P) and also depend on the reference state. They can be expressed as

$$a_A = \gamma_A x_A , \ a_B = \gamma_B x_B , \tag{2.12}$$

with γ_A, γ_B the activity coefficients.

The simplest solutions are those for which (choosing Raoultian reference states)

$$\gamma_A \equiv 1 , \ \gamma_B \equiv 1 , \tag{2.13}$$

called <u>ideal solutions</u>, and then $a_i = x_i$, i = A,B. For ideal solutions we have (see Appendix A):

$$\Delta\bar{\mu}^{id} = RT \ln x_i \tag{2.14}$$

$$\Delta g^{id} = RT[x_A \ln x_A + x_B \ln x_B] = RT[(1 - x)\ln(1 - x) + x\ln x] < 0, \tag{2.15}$$

$$\Delta h^{id} = 0 \tag{2.16}$$

$$\Delta s^{id} = -R[x_A \ln x_A + x_B \ln x_B] = -R[(1 - x)\ln(1 - x) + x\ln x] > 0, \tag{2.17}$$

$$\Delta v^{id} = 0 \tag{2.18}$$

$$\Delta c_p^{id} = 0 \tag{2.19}$$

It is convenient then to express mixing functions of real solutions as sums of ideal and excess terms:

$$\Delta w^{mix} = \Delta w^{id} + \Delta w^{ex} \ . \tag{2.20}$$

Since $\Delta w^{mix} = \sum_i x_i \, \Delta \bar{w}_i^{mix}$, we also have

$$\Delta \bar{w}_i^{mix} = \Delta w_i^{id} + \Delta w_i^{ex} \ , \ i = A,B \ , \tag{2.21}$$

for the partial properties. Again, all excess functions (partial and integral) may be expressed in terms of Δg^{ex} (see Appendix and Sect. 3). The ideal terms being known, a complete thermodynamic model of the alloy consists of an expression for the excess Gibbs free energy (of mixing) which describes the interaction of the components.

Clearly, each phase (solid, liquid) constitutes a different chemical solution and the discussion above applies to any single phase. To distinguish between values for different phases, we shall use a superscript $j = S,L$. In particular, different expressions for $\Delta g^{ex,S}$ and $\Delta g^{ex,L}$ may be necessary.

3. PARTIAL AND INTEGRAL PROPERTIES

From the discussion on mixing in Sect. 2, it follows that the value of a thermodynamic function w at state (x,T,P) (in a fixed single phase) is given by

$$\begin{aligned} w(x,T,P) &= w^{o}(x,T,P) + \Delta w^{mix}(x,T,P) \\ &= w^{o}(x,T,P) + \Delta w^{id}(x,T,P) + \Delta w^{ex}(x,T,P) \ , \end{aligned} \tag{3.1}$$

and similarly for partial values,

$$\begin{aligned} \overline{w}_i(x,T,P) &= w_i^{o}(T,P) + \Delta\overline{w}(x,T,P) \\ &= w_i^{o}(T,P) + \Delta\overline{w}_i^{id} + \Delta\overline{w}_i^{ex} \ , \ i = A,B \ . \end{aligned} \tag{3.2}$$

At the same time, the integral and partial properties are related by

$$w(x,T,P) = \sum_i x_i \ \overline{w}_i(x,T,P) = (1 - x) \ \overline{w}_A + x \ \overline{w}_B \ , \tag{3.3}$$

or, conversely,

$$\overline{w}_A = w - x\left(\frac{\partial w}{\partial x}\right)_{T,P} \quad \text{or} \quad \overline{w}_B = w + (1-x) \left(\frac{\partial w}{\partial x}\right)_{T,P} \ . \tag{3.4}$$

In particular, for the chemical potential and the Gibbs free energy we have,

$$\begin{aligned} \overline{\mu}_i(x,T,P) &= \mu_i^{o}(T,P) + \Delta\overline{\mu}_i^{id} + \Delta\overline{\mu}_i^{ex} \\ &= \mu_i^{o} + RT \ln x_i + RT \ln \gamma_i \ , \ i = A,B \ , \end{aligned} \tag{3.5}$$

$$\begin{aligned} g(x,T,P) &= g^{o}(T,P) + \Delta g^{id} + \Delta g^{ex} \\ &= \sum_i x_i \ \overline{\mu}_i \\ &= \sum x_i \overline{\mu}_i^{o} + RT \sum x_i \ \ln x_i + RT \sum x_i \ \ln \gamma_i \end{aligned} \tag{3.6}$$

Finding the reference values $w_i^{o}(T,P)$ is discussed in the next section. The ideal values are known [see (2.14) - 2.19)] and the excess values of w = h, s, v, c_p can be expressed in terms of Δg_i^{ex} or more

conveniently in terms of excess chemical potentials via partial properties (see Sect. 5). The formulae are as follows:

Partial enthalpies:
$$\bar{h}_i(x,T,P) = h_i^o(T,P) + 0 + \Delta\bar{h}_i^{ex}$$
$$= h_i^o + \left[\frac{\partial\left(\frac{\Delta\bar{\mu}_i^{ex}}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_{x,P}, \quad i = A,B \,. \tag{3.7}$$

Integral enthalpy:
$$h(x,T,P) = h^o(x,T,P) + 0 + \Delta h^{ex}$$
$$= \sum x_i\bar{h}_i \tag{3.8}$$
$$= h^o + \left[\frac{\partial\left(\frac{\Delta g^{ex}}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_{x,P} \,.$$

Partial entropies:
$$\bar{s}_i(x,T,P) = s_i^o(T,P) + \Delta\bar{s}_i^{id} + \Delta\bar{s}_i^{ex} \tag{3.9}$$
$$= s_i^o - R\ln x_i - \left(\frac{\partial\bar{\mu}_i^{ex}}{\partial T}\right)_{x,P}, \quad i = A,B$$

Integral entropy:
$$s(x,T,P) = s^o(x,T,P) + \Delta s^{id} + \Delta s^{ex} \tag{3.10}$$
$$= \sum x_i\bar{s}_i$$
$$= s^o - R\sum_i x_i \ln x_i - \left(\frac{\partial\Delta g^{ex}}{\partial T}\right)_{x,P} \,.$$

Partial volumes:
$$\bar{v}_i(x,T,P) = v_i^o(T,P) + 0 + \Delta\bar{v}_i^{ex} \tag{3.11}$$
$$= v_i^o + \left(\frac{\partial\Delta\bar{\mu}_i^{ex}}{\partial P}\right)_{x,T}, \quad i = A,B \,.$$

Integral volume:

$$v(x,T,P) = v^o(x,T,P) + 0 + \Delta v^{ex}$$

$$= \sum x_i \bar{v}_i \tag{3.12}$$

$$= v^o + \left(\frac{\partial \Delta g^{ex}}{\partial P}\right)_{x,T} .$$

Partial heat capacities:

$$\bar{c}_{pi}(x,T,P) = c^o_{pi}(T,P) + 0 + \Delta \bar{c}^{ex}_{pi}$$

$$= c^o_{pi} + \left(\frac{\partial \Delta \bar{h}^{ex}_i}{\partial T}\right)_{x,P} \tag{3.13}$$

$$= c^o_{pi} - T\left(\frac{\partial^2 \Delta \bar{\mu}^{ex}_i}{\partial T^2}\right)_{x,p} , \quad i = A,B .$$

Integral heat capacity:

$$c_p(x,T,P) = c^o_p\ (x,T,P) + 0 + \Delta c^{ex}_p = \sum x_i \bar{c}_{pi}$$

$$= c^o_p + \left(\frac{\partial \Delta h^{ex}}{\partial T}\right)_{x,P} \tag{3.14}$$

$$= c^o_p - T\left(\frac{\partial^2 \Delta h^{ex}}{\partial T^2}\right)_{x,P} .$$

These are standard thermodynamic relations valid for each single phase, solid and liquid. For a state (x,T,P) which lies in a two-phase region of the phase diagram, the thermodynamic properties per mole of A plus B are averages of the corresponding liquidus and solidus values weighted by the liquid fraction, λ.

Let us use superscripts S, L, and m to denote values for solid, liquid and two-phased (mushy) states, respectively. In particular, $x^S(T)$ and $x^L(T)$ denote the solidus and liquidus compositions at temperature T. For a simple phase diagram like that for GeSi,[4] shown in Fig. 1, the liquid fraction at mean composition x and temperature T, when (x,T) lies in the two-phase region, is given by the lever rule

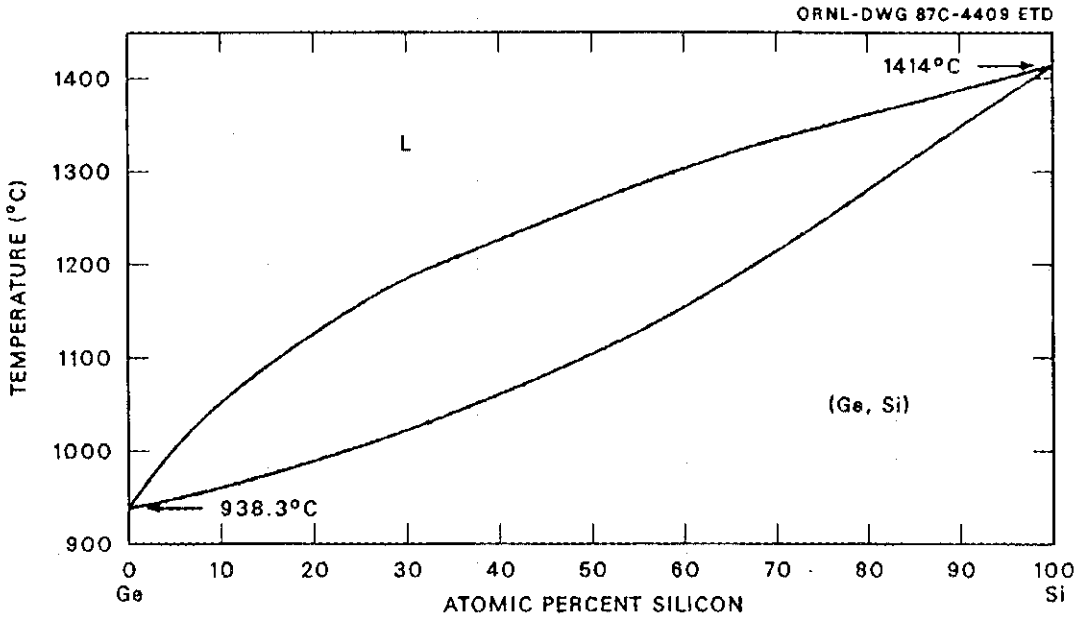

Fig. 1. Germanium-silicon phase diagram.[4]

$$\lambda(x,T) = \frac{x^S(T) - x}{x^S(T) - x^L(T)} \quad . \tag{3.15}$$

Then, the value of a property $w(x,T,P)$ for a two-phase (mushy) state (x,T,P) is

$$w^m(x,T,P) = \lambda w^L(x^L(T),T,P) + (1 - \lambda)\, w^S(x^S(T),T,P) \quad . \tag{3.16}$$

Using the above formulae, values at any state can be calculated once the reference values and the excess free energy are found.

4. EVALUATION OF REFERENCE VALUES

The required reference values are $w_A^{o,j}(T,p)$ and $w_B^{o,j}(T,p)$ for the pure components A and B in each single phase j = S,L. Usually the pressure is fixed at P_{atm}, and using the thermodynamic relations listed in the Appendix, only the following standard thermodynamic data for each component i = A,B are needed:

T_i = melt temperature of i = A,B,

$\Delta h_i^{o,fus}(T_i)$ = molar heat of fusion of i at its melt temperature T_i,

$s_i^o(T_{ref})$ = standard molar entropy of i at some reference temperature T_{ref} (usually T_{ref} = 298.15 K),

$c_{pi}^{o,j}(T)$ = molar heat capacity of i in phase j as function of temperature.

From these, we obtain (assuming $T_{ref} < T_i$ for definiteness)

$$h_i^{o,S}(T) = \int_{T_{ref}}^{T} c_{pi}^{o,S}(T)dT \ , \ T < T_i \ , \qquad (4.1)_S$$

$$h_i^{o,L}(T) = h_i^{o,S}(T_i) + \Delta h_i^{o,fus}(T_i) + \int_{T_i}^{T} c_{pi}^{o,L}(T)dT \ , \ T > T_i \ , \qquad (4.1)_L$$

$$s_i^{o,S}(T) = s_i^o(T_{ref}) + \int_{T_{ref}}^{T} \frac{1}{t} c_{pi}^{o,S}(t)\, dt, \ T < T_i \ , \qquad (4.2)_S$$

$$s_i^{o,L}(T) = s_i^{o,S}(T_i) + \frac{1}{T_i} \Delta h_i^{o,fus}(T_i) + \int_{T_i}^{T} \frac{1}{t} c_{pi}^{o,L}(t)\, dt \ , \ T > T_i \qquad (4.2)_L$$

$$\mu_i^{o,S}(T) = h_i^{o,S}(T) - T\, s_i^{o,S}(T) \ , \ T < T_i \ , \qquad (4.3)_S$$

$$\mu_i^{o,L}(T) = h_i^{o,L}(T) - T\, s_i^{o,L}(T) \ , \ T > T_i \ . \qquad (4.3)_L$$

These are the reference values for the partial properties entering the formulae of Sect. 3 when $P \equiv P_{atm}$. In the (unlikely) case that the pressure dependence of the basic data is significant and can be found, one can also determine

$$v_i^{o,j}(T,P) = \left[\frac{\partial \mu_i^{o,j}(T,P)}{\partial P}\right]_T , \quad j = S,L , \quad i = A,B . \tag{4.4}$$

More effectively, however, the temperature dependence of the molar volumes can be found from the (isobaric) thermal expansion coefficients

$$\alpha_i^{o,j}(T,P) = \frac{1}{v_i^{o,j}} \left(\frac{\partial v_i^{o,j}}{\partial T}\right)_P , \quad i = A,B , \quad j = S,L . \tag{4.5}$$

Dropping the implied pressure dependence and integrating Eq. (4.5), we have

$$v_i^{o,j}(T) = v_i^{o,j}(T_{ref})\, e^{\int_{T_{ref}}^{T} \alpha_i^{o,j}\, dT} , \quad i = A,B , \quad j = S,L \tag{4.6}$$

with T_{ref} a reference temperature, typically = 300 K, at which reference molar volumes can be found. Usually the thermal expansion coefficients are small and approximately constant for solids, so (4.6) may be approximated by

$$v_i^{o,S} = v_i^{o,S}(T_{ref})\, [1 + \alpha_i^{o,S} \quad (T - T_{ref})] , \quad i = A,B . \tag{4.7}$$

To find the liquid molar volume relative to its value at the standard state, we also need the volume change upon melting,

$$\Delta v_i^o(T_i) = v_i^{o,L}(T_i) - v_i^{o,S}(T_i) .$$

Then

$$v_i^{o,L}(T) = v_i^{o,S}(T_i) + \Delta v_i^o(T_i) + v_i^{o,L}(T_i)\, e^{\int_{T_i}^{T} \alpha_i^{o,L} dT}$$

$$= v_i^{o,L}(T_i) \left[1 + e^{\int_{T_i}^{T} \alpha_i^{o,L} dT}\right] ,$$

or, writing

$$v_i^{o,L} = v_i^{o,s} + \Delta v_i^o$$

and approximating the exponential, yields

$$v_i^{o,L}(T) \approx [v_i^{o,S}(T_i) + \Delta v_i^o(T_i)][2 + \alpha_i^{o,L} \cdot (T - T_i)] \ , \ i = A,B \ . \quad (4.8)$$

5. EXCESS FREE ENERGY

In Sect. 3 all property values are expressed in terms of the excess free energy Δg^{ex} or excess chemical potentials $\Delta\bar{\mu}_i^{ex}$. These quantities describe the interaction of the two pure components and constitute a thermodynamic model of each phase of the alloy or solution. If $\Delta\bar{\mu}_i^{ex,j}$, $i = A,B$, $j = S,L$ are known as functions of (x,T) at a fixed pressure P, then the solidus, $x^S(T)$, and liquidus, $x^L(T)$, at that pressure are described by the equations

$$\bar{\mu}_A^S(x^S,T) = \bar{\mu}_A^L(x^L,T) \tag{5.1)A}$$

$$\bar{\mu}_B^S(x^S,T) = \bar{\mu}_B^L(x^L,T) \tag{5.1)B}$$

expressing thermodynamic equilibrium between the two phases. From Eq. (3.3), the partial molar chemical potentials of the liquid and solid phases are related to the pure element reference value, the phase composition and the excess due to non-idealities in the mixing process:

$$\mu_A^{o,S}(T) + RT\ln(1-x^S) + \Delta\bar{\mu}_A^{ex,S}(x^S,T) = \mu_A^{o,L}(T) + RT\ln(1-x^L) + \Delta\bar{\mu}_A^{ex,L}(x^L,T) \tag{5.2)A}$$

$$\mu_B^{o,S}(T) + RT\ln x^S + \Delta\bar{\mu}_B^{ex,S}(x^S,T) = \mu_B^{o,L}(T) + RT\ln x^L + \Delta\bar{\mu}_B^{ex,L}(x^L,T) \tag{5.2)B}$$

Equations (5.2)A and (5.2)B provide the relations between the shape of the phase diagram, as x^S and x^L, and the chemical consequence of the mixing process as defined by the four partial molar chemical potentials. If these are known from measurements, then Eq. (5.2) may be used to determine the shape of the phase diagram. The converse process is of interest here where known values of x^S and x^L taken from a phase diagram are used to determine the properties of mixing.

Since Eqs. (5.2)A and (5.2)B provide only two relationships for the four unknown mixing properties $\bar{\mu}_A^{ex,S}$, $\bar{\mu}_A^{ex,L}$, $\bar{\mu}_B^{ex,S}$, and $\bar{\mu}_B^{ex,L}$, additional information must be provided for the determination from the chemical nature of the solution. For example, the solution may be represented as ideal, in which case the excess terms in Eq. (5.2) are zero

and the relationships (2.14) through (2.19) may be used for determination of the mixing properties.

The simplest real solutions, called regular solutions,[2] are described by a single interaction term:

$$\Delta g^{ex}(x,T) = \Omega\, x_A x_B \tag{5.3}$$

$$= \Omega\,(1 - x)\, x\ .$$

To allow higher order interactions one writes

$$\Delta g^{ex}(x,T) = \sum_{m,n} \Omega_{mn}\, x_A^m\, x_B^n\ , \tag{5.4}$$

where the interaction coefficients Ω_{mn} must be determined by fitting experimental data. An extensive discussion on excess free energy representation may be found in Lupis.[1]

Estimation of the interaction coefficients defined in Eqs. (5.3) or (5.4) from the phase diagram may be performed by use of a computer package like FITBIN[3] by the following procedure:

Step 1: Choose a particular number of interaction terms, say

$$\Delta g^{ex} = \Omega_{11}\, x_A x_B + \Omega_{12}\, x_A x_B^2 + \Omega_{21}\, x_A^2 x_B + \Omega_{22}\, x_A^2 x_B^2\ .$$

Step 2: Use a computer package (e.g. FITBIN) to calculate the unknown interaction coefficients by using known solidus and liquidus composition data from the phase diagram. The FITBIN program is based on relationships such as Eq. (5.2A) and (5.2B) where the excess terms are estimated in terms of the unknown interaction coefficients. A sufficient number of points (x^S and x^L) on the phase diagram are selected to enable a least squares fit for the unknown interaction coefficients.

Step 3: Redetermine the phase diagram using the estimated interaction coefficients. If the resulting phase diagram is not sufficiently close to the known phase diagram, then return to Step 1 and allow more interaction terms.

Step 4: Repeat until a satisfactory fit is obtained. The computer package calculates the interaction coefficients and thus an expression for Δg^{ex} is obtained.

6. DETERMINATION OF THE ENTHALPY OF Ge-Si ALLOYS

We apply the described procedure to the Ge-Si system in order to find the enthalpy h(x,T) and therefore enable prediction for the enthalpy difference between any two states.

According to Massalski,[4] Ge and Si form regular liquid and solid solutions with interaction coefficients,

$\Omega^L = 3500$ (J/mol) and

$\Omega^S = 6500$ (J/mol) .

The phase diagram for this system is shown in Fig. 1. Some pertinent thermochemical properties of the pure materials are given in Table 1.

Table 1. Heat storage properties of Ge and Si

		Ge	Si
Molecular weight	g/mol	72.59	28.09
Melting point	K	1213	1687
Heat of fusion	J/g	507	1802
	J/cm^3 at T_m	2649	4116
Interaction coefficients[a]	J/mole		
Solid solution		6500	
Liquid solution		3500	

[a]Defined by Eq. (5.3) for regular solutions.

The required data for the pure materials, A = Ge and B = Si are available in Kubaschewski and Alcock.[5]

Melt temperature (K): $T_A = 1211$, $T_B = 1687$

Heat of Fusion (cal/mol): $\Delta h_A^{o,fus}(T_A) = 8800$,

$\Delta h_B^{o,fus}(T_B) = 12,100$

Standard entropy (cal/mol K): $s_A^o(T_{ref}) = 7.43$, $T_{ref} = 298$ K

$s_B^o(T_{ref}) = 4.5$

Solid heat capacity (cal/mol K): $c_{pA}^{o,S}(T) = 5.16 + 1.4\ (T/10^3)$

$c_{pB}^{o,S}(T) = 5.72 + 0.59\ (T/10^3)$

$- 0.99*10^5/T^2$

Liquid heat capacity (cal/mol K): $c_{pA}^{o,L}(T) = 6.6$

$c_{pB}^{o,L}(T) = 6.12$

For regular solutions with interaction coefficients $\Omega^S = 6500$ J/mol (1554 cal/mol) and $\Omega^L = 3500$ J/mol (837 cal/mol) we obtain,

$$\Delta g^{ex,S} = \Omega^S(1-x)x \quad , \quad \Delta g^{ex,L} = \Omega^L(1-x)x \ , \tag{6.1}$$

and, by (3.4), the excess chemical potentials are (in cal/mol)

$$\begin{aligned} \Delta\bar{\mu}_A^{ex,S} &= \Omega^S x^2 \quad , \quad \Delta\bar{\mu}_B^{ex,S} = \Omega^S(1-x)^2 \ , \\ \Delta\bar{\mu}_A^{ex,L} &= \Omega^L x^2 \quad , \quad \Delta\bar{\mu}_B^{ex,L} = \Omega^L x^2 \ . \end{aligned} \tag{6.2}$$

Now we use (3.7) to find the partial enthalpies (in cal/mol):

$$\begin{aligned} \bar{h}_A^S(x,T) &= h_A^{o,S}(T) + \Omega^S x^2 \\ \bar{h}_B^S(x,T) &= h_B^{o,S}(T) + \Omega^S(1-x)^2 \\ \bar{h}_A^L(x,T) &= h_A^{o,L}(T) + \Omega^L x^2 \\ \bar{h}_B^L(T) &= h_B^{o,L}(T) + \Omega^L(1-x)^2 \ , \end{aligned} \tag{6.3}$$

where the reference values are obtained by integration of the heat

capacities according to (4.1):

$$
\begin{aligned}
h_A^{o,S}(T) &= -1600.675 + 5160\left(\frac{T}{10^3}\right) + 700\left(\frac{T}{10^3}\right)^2 , \\
h_B^{o,S}(T) &= -2063.69 + 5720\left(\frac{T}{10^3}\right) + 295\left(\frac{T}{10^3}\right)^2 + 99\left(\frac{10^3}{T}\right), \\
h_A^{o,L}(T) &= 6481.897 + 6600\left(\frac{T}{10^3}\right) , \\
h_B^{o,L}(T) &= 10258.635 + 6120\left(\frac{T}{10^3}\right) .
\end{aligned}
\tag{6.4}
$$

Then, using (3.3), the integral molar enthalpies are

$$
\begin{aligned}
h^S(x,T) &= (1-x)\ \bar{h}_A^S(x,T) + x\ \bar{h}_B^S(x,T) , \quad \text{(in solid)} \\
h^L(x,T) &= (1-x)\ \bar{h}_A^L(x,T) + x\ \bar{h}_B^L(x,T) , \quad \text{(in liquid)}
\end{aligned}
\tag{6.5}
$$

and, by (3.16)

$$
h^m(x,T) = \lambda(x,T)\ h^L[x^L(T),T] + [1-\lambda(x,T)]\ h^S[x^S(T),\ T] \tag{6.6}
$$

in the two-phase ("mushy") region, where

$$
\lambda(x,T) = \frac{x^S(T) - x}{x^S(T) - x^L(T)} , \tag{6.7}
$$

$x^S(T)$ and $x^L(T)$ being the solidus and liquidus compositions. For calculations we need numerical values for x^S, x^L. Reading 10-12 points for each curve off the phase diagram and employing a least-squares curve-fitting routine to fit the points, we obtained the following expressions (with $T_o = (T - T_A)/(T_B - T_A)$):

$$
\begin{aligned}
x^S(T) &= .63275\ T_o - .98298\ T_o^2 + .50489\ T_o^3 + 1.2199\ \ln(1 + T_o) , \\
x^L(T) &= .245374\ T_o + .61952\ T_o^2 - .0848\ T_o^3 + .22\ T_o^4 .
\end{aligned}
\tag{6.8}
$$

Relative to the input data points, the maximum relative error was less than .9% for $x^S(T)$ and .5% for $x^L(T)$.

The above expressions yield the enthalpy in terms of cal/mol. More conveniently, we will express results in terms of joules per unit mass

and joules per unit volume. Conversion of h(cal/mol) to h(kJ/kg) is accomplished by multiplying by 4.184/M(x), where M(x) is the alloy molecular weight at composition x. Alternatively, to express the values in J/cm^3, multiply by $4.184/v^j(x,T,P)$, where v^j (x,T,P) is the molar volume of the alloy at state (x,T,P) in phase j = S,m,L. This is expressed as follows:

By (3.12)

$$v^j(x,T,P) = (1-x)\bar{v}_A^j + x\,\bar{v}_B^j \quad , \quad j = S,L \ , \tag{6.9}$$

where, by (3.11), the partial molar volumes are

$$\bar{v}_i^j(s,T,P) = v_i^{o,j}(T,P) + \left(\frac{\partial \Delta\bar{\mu}_i^{ex,j}}{\partial P}\right)_{x,T} \ , \ i = A,B \ , \ j = S,L \ . \tag{6.10}$$

Dropping the pressure dependence of the excess chemical potentials, and to be consistent with (6.2), we take the last terms as zeros. The reference values are found by (4.7) and (4.8). From [6],

$$v_A^{o,S}(T_{ref},P_{atm}) = 13.6 \ cm^3/mol \quad , \quad v_B^{o,S}(T_{ref},P_{atm}) = 12.1 \ cm^3/mol$$

at T_{ref} = 300 K, and from [7],

$$\alpha_A^{o,S}(T) = 3 \times 7.5 \times 10^{-6}/K \ , \ 723 \ K \leqslant T \leqslant 1113 \ K \ ,$$

$$\alpha_B^{o,S}(T) = \begin{cases} 3 \times 3.0 \times 10^{-6}/K \ , \ 773 \ K \leqslant T \leqslant 1113 \ K \ , \\ 3 \times 3.3 \times 10^{-6}/K \ , \ T = 1273 \ . \end{cases}$$

We assume these values hold at temperatures up to 1700 K, whence, in the range 1200 K $\leqslant$ T $\leqslant$ 1700 K, we take

$$\bar{v}_A^{S \text{ or } L}(T) \approx v_A^{o,S \text{ or } L}(T) \approx (13.6)[1 + 22.5 \times 10^{-6})(T - 300)] \ , \tag{6.11}$$

$$\bar{v}_B^{S \text{ or } L}(T) \approx v_B^{o,S \text{ or } L}(T) \approx v_B^{o,S}(1200)[1 + (9.9 \times 10^{-6})(T - 1200)] \ , \tag{6.12}$$

with

$$v_B^{o,S}(1200) \approx (12.1)[1 + (9 \times 10^{-6})(1200 - 300)] = 12.198 \text{ cm}^3/\text{mol}.$$

Evaluation of the solid and liquid phase molar enthalpies, as expressed by Eq. (6.5), and the molar enthalpies in the two phase regime, according to Eq. (6.6), was implemented by a short Fortran program listed in Appendix B. Figures 2 and 3 express the resulting specific enthalpies vs. composition and temperature, respectively; Figs. 4 and 5 express results in terms of enthalpy per unit volume.

One measure of the heat storage capacity of GeSi alloys is the enthalpy change of a particular composition between the liquidus and solidus temperatures. These may be determined most conveniently using Figs. 3 and 5 for the specific and volumetric enthalpy changes, respectively. Values are listed in Table 2 in columns 5 and 6 for a range of alloy compositions. As expected, both the specific enthalpy and

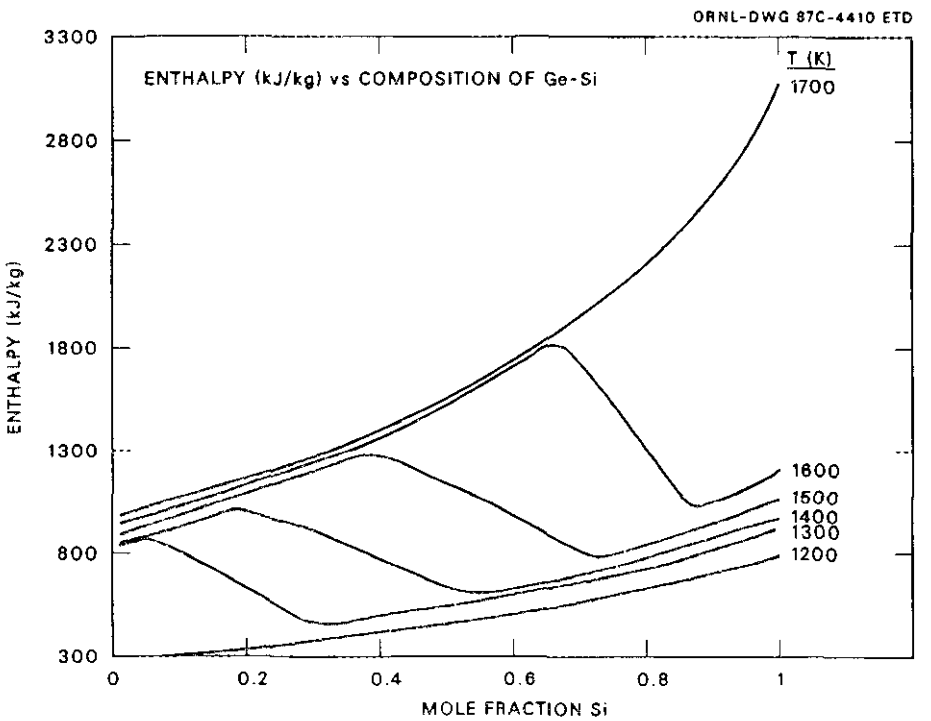

Fig. 2. Specific Enthalpy (kJ/kg) vs GeSi composition.

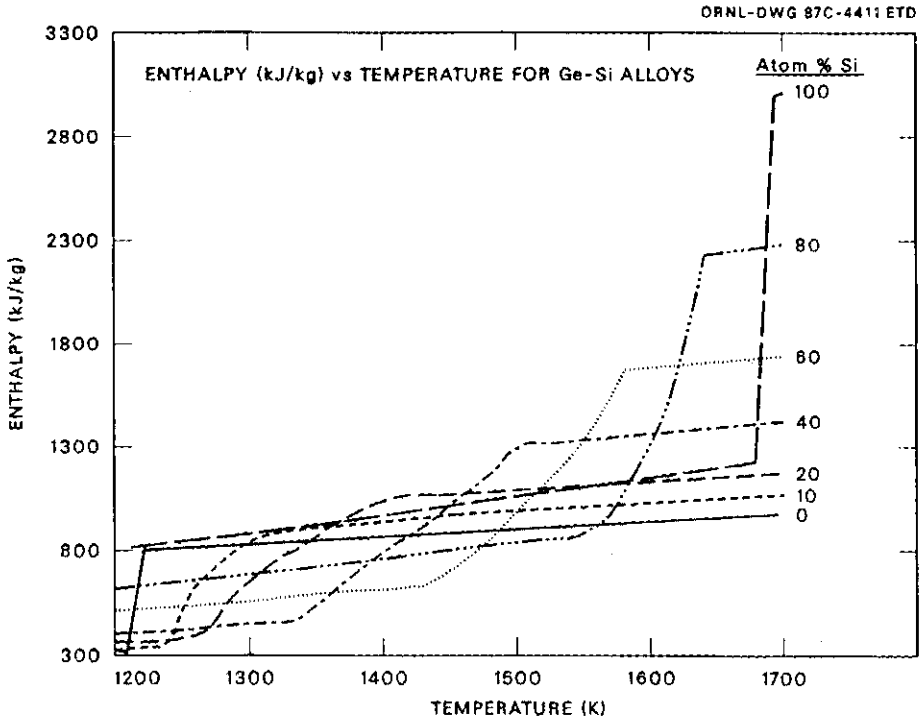

Fig. 3. Specific enthalpy (kJ/kg) vs temperature.

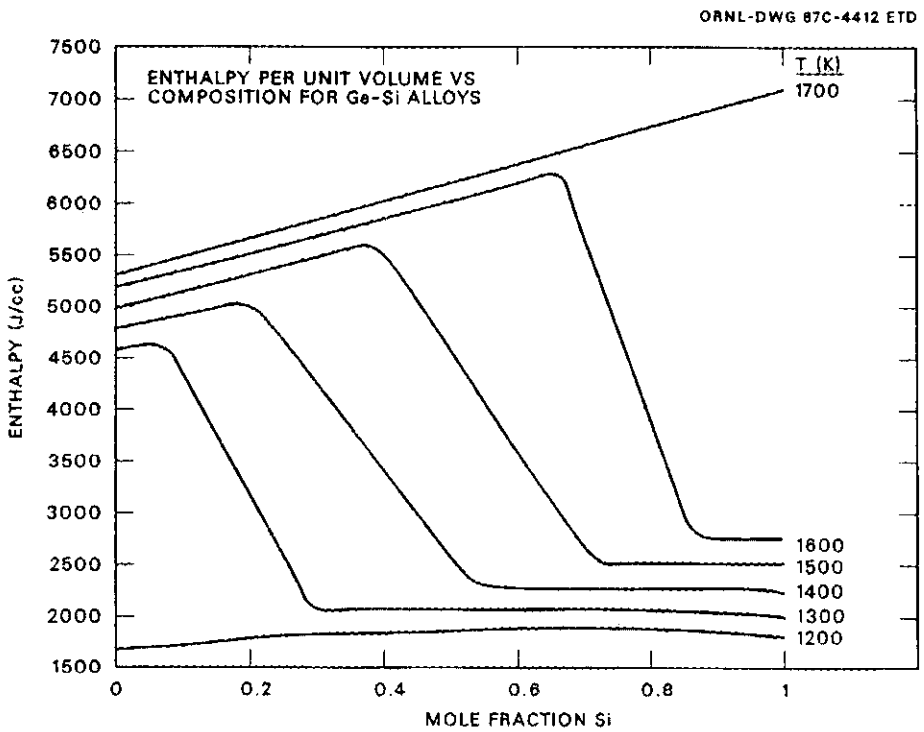

Fig. 4. Enthalpy per unit volume (J/cm^3) vs composition.

Table 2. Estimated heat storage capacities of Ge-Si alloys per 100 K ΔT

Mole fraction Si	Solidus temperature (K)	Solidus temperature (K)	ΔT between liquidus and solidus (K)	Enthalpy change between liquidus and solidus		Enthalpy change per 100 K ΔT	
				(J/g)	(J/cm^3)	(J/g)	(J/cm^3)
0	1211	1211	0	507	2649	507	2649
0.2	1265	1403	138	650	3140	471	2270
0.4	1337	1503	166	830	3450	500	2080
0.6	1451	1573	122	1130	3690	926	3020
0.8	1553	1663	110	1330	3930	1210	3570
1.0	1687	1687	0	1802	4116	1802	4116

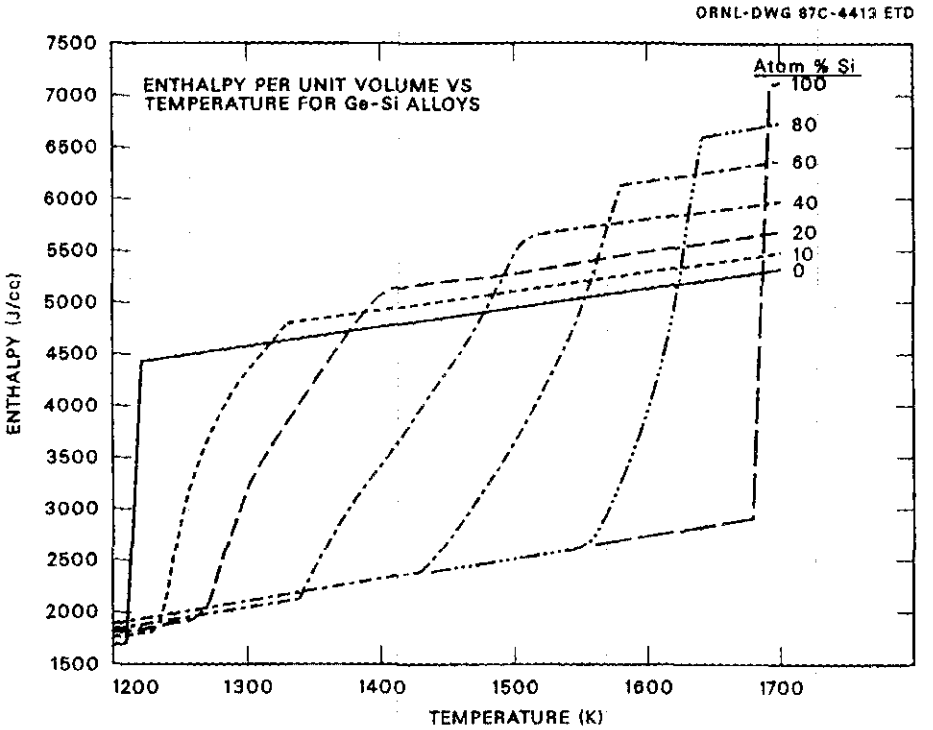

Fig. 5. Enthalpy per unit volume (J/cm^3) vs temperature.

volumetric enthalpy changes between the liquidus and solidus temperatures increase with increasing Si contents reflecting the intrinsically higher values for Si.

However, the increase in specific heat storage capacity with increasing Si content of the alloy is less than expected for Ge-rich compositions. For example, the change from pure Ge to Ge-20 atom-% Si increases the specific enthalpy changes only 28% whereas a 51% increase would be expected were the increase proportional to the Si content over the span of composition. That is, the full benefit of the high specific enthalpy of Si is felt predominantly at the Si-rich end of the scale.

Conversely, Si additions contribute more than proportionately to the volumetric enthalpy change for Ge-rich compositions. That is, addition of Si to Ge of 20 atom-% increases the volumetric heat storage 19% compared with only 11% were the increase to occur proportionately.

An additional measure of heat storage capability for non-congruently melting alloys could be defined as the enthalpy changes per

some specified ΔT between the liquidus and solidus temperatures. A PCM operating in this mode would never completely freeze or melt. Columns 7 and 8 of Table 2 list the specific and volumetric enthalpy change per 100 K ΔT in the two-phase regime for a range of compositions. On this basis we see that both the specific and volumetric heat storage capabilities predicted to fall somewhat by addition of Si to Ge-rich compositions. The reason for this appears to be the higher endothermic heat required to form the solid solution relative to the liquid solution. That is for Ge-rich compositions, the exothermic solidification process is partially quenched by the heat required to form the solid solution, as evidenced by the higher interaction coefficient for the solid relative to the liquid solution.

Above a Si mole fraction of 0.5, the higher specific heat storage of Si begins to affect a general rise in storage capacity from ~500 kJ/kg for a 100 K swing in temperature at $x = 0.4$ to the value of 1802 (kJ/kg) for pure Si.

7. CONCLUSIONS

This report represents an initial step in the evaluation of Ge-Si alloys as heat storage materials for solar dynamic power systems. Since these are not congruently melting alloys, an estimation of the enthalpy changes for a given temperature swing in the two phase regime of the alloy must account for the heats of solution of both the solid and the liquid phase. Development of the capability for determining this enthalpy change per unit mass and also on a volumetric basis is the primary purpose of this report. This was accomplished by development of a calculational procedure based on the chemical thermodynamics of non-ideal solutions following the principals outlined in Lupis,[1] handbook values for the pure components Ge and Si, and the reported "regular" nature of both solid and liquid Ge-Si solutions.[4]

The calculations are developed in a general way so that estimation of any of the other thermodynamic properties of Ge-Si alloys, for example the Gibbs free energy as a function of temperature and composition, may be acquired with only minor variations in the Fortran program listed in Appendix B. In addition, the procedures required for extension of the estimation method to systems of non-regular solutions but for which the equilibrium phase diagram is available may readily be accomplished with the aid of the FITBIN curve fitting package available in FACT.[3]

A preliminary review of the results shown in Figs. 2 through 5 and in Table 2 show that addition of Si to Ge has an initial effect of reducing the heat storage capability somewhat due to the relative large endothermic heat required to form the solid solution relative to the liquid solution. These comparisons are shown in Table 2 based on an assumed temperature swing of 100 K in the two-phase region. For compositions above 50% Si, both specific and volumetric capacities rise rapidly with Si content to the high values representative of pure Si.

The use of Ge-Si alloys for heat storage in solar receivers has both negative and positive aspects which have not yet been fully evaluated. The negative aspects relate to the non-congruent nature of the phase change process which requires that the heat delivery occurs over

some temperature range and also requires movement of constituents between liquid and solid phases. It is not yet clear how much of a detriment these factors present. The ideal of isothermal heat delivery for congruently melting PCMs is after all never achieved, with temperature swings of ±50 K estimated in some cases for salts in high heat flux zones required for thermal transport.

On the other hand, some positive aspects of using this alloy system for solar receiver heat storage are readily apparent which warrant its evaluation. The alloy system provides a range of heat storage temperatures from 1213 to 1687 K by variation of only the composition. Their high thermal conductance and relatively small volume change on melting are additional potential benefits.

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APPENDIX A

BASIC RELATIONS FOR g, h, s, v, AND c_p:

$$g = h - Ts \ ,$$

$$h = g - T\left(\frac{\partial g}{\partial T}\right)_{x,P} = \left[\frac{\partial\left(\frac{g}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_{x,P} \ ,$$

$$s = \frac{h - g}{T} = \frac{g}{T} - \left(\frac{\partial g}{\partial T}\right)_{x,p} \ ,$$

$$v = \left(\frac{\partial g}{\partial P}\right)_{x,T} \ ,$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_{x,P} = T\left(\frac{\partial s}{\partial T}\right)_{x,P} = -T\left(\frac{\partial^2 g}{\partial T^2}\right)_{x,P} \ .$$

The last four formulae express h, s, v, c_p in terms of g. They remain valid for relative as well as partial quantities. For example,

$$\Delta h^{mix} = \Delta g^{mix} - T\left(\frac{\partial \Delta g^{mix}}{\partial T}\right)_{x,P} \ , \text{ and}$$

$$\Delta \bar{h}_i = \Delta \bar{\mu}_i - T\left(\frac{\partial \Delta \bar{\mu}_i}{\partial T}\right)_{x,P}$$

For a pure material, the enthalpy and entropy at any temperature can be found by integration of

$$c_p = \left(\frac{\partial h}{\partial T}\right)_P \text{ and } c_p = T\left(\frac{\partial s}{\partial T}\right)_P$$

respectively, as is done in Sect. 4.

APPENDIX B

PROGRAM LISTING FOR THE DETERMINATION OF THE ENTHALPIES PER UNIT MASS AND VOLUME OF SILICON-GERMANIUM ALLOYS

```
c 8/05/87   h.f       Enthalpy of Ge-Si  as function of (x,T)
c....       This version outputs  x  h(x,T) in  J/cc  or in  kJ/kg
c....            for 50 values of x, 0 <= x <= 1,  for each given  T.
c....       Phases treated as regular solutions [ Massalski,1986 ].
c....       Computed enthalpies in cal/mol, Temperatures in degK.
c.... x = mole fraction of B=Si,  xL(T)=liquidus,  xS(T)=solidus
c.... wx = molecular weight of alloy at composition x  (g/mol)
c.... vx = molar volume of alloy at x
c.... zlam(x,T) = liquid fraction (from lever rule)
c.... h0JI(T) (J=L,S, I=A,B): reference molar enthalpy of I in phase J.
c.... omegaL,omegaS : regular solution model interaction coefficients.
c......required input: single value of Temperature;
c........     outputs: x  h(x,T) in J/cc, in standard output file,
c........             : x  h(x,T) in kJ/kg, in output file 7.
10       read(5,*) T
c.........................
         do 1000 n=0,50
           x=.02*n
          call PHASE(x,T,xL,xS,zlam)
c........
         if( zlam .le. 0. ) then
          call ENTHALS(x,T,h)
           goto 100
c........
         else if( zlam .lt. 1.) then
          call ENTHALm(x,T,xL,xS,zlam,h)
             goto 100
c.........
        else
           call ENTHALL(x,T,h)
            goto 100
         endif
100     continue
c..............find the molar volume vx=v(x,T,P)
          vxA = 13.6*(1+22.5e-6*(T-300))
          vxB = 12.1*(1+9.9e-6*(T-300))
           vx = (1-x) * vxA + x * vxB
c..............convert cal/mol to J/cc = (cal/mol)*4.184/vx
          hvol = h * 4.184 / vx
         write(6,555) x,hvol
c..............find the molecular weight wx
           wx = 75.59*(1-x) + 28.086*x
c..............convert cal/mol to kJ/kg = J/g = (cal/mol)*4.184/wx
       hweight = h * 4.184 / wx
        write(7,555) x,hweight
c...............................
1000     continue
c.........................................
555    format(f10.6,f15.5)
999    stop
       end
c-----------------------------------------------------------------
        subroutine PHASE(x,T,xL,xS,zlam)
c..........given x,T, find xL, xS and zlam=liquid fraction:
c..........TA,TB from phase diagram (instead of 1210.4 and 1685)
        TA = 1211.45
        TB = 1687.15
        T0 = (T - TA)/(TB - TA)
         if( T .gt. TA ) goto 200
          xL = 0.
          xS = 0.
          zlam = 0.
          goto 500
200      if( T .lt. TB ) goto 300
          xL = 1.
          xS = 1.
          zlam = 1.
          goto 500
300      continue
```

```
c..........xL,xS from fitting the phase diagram (in degC)
c..........to within .5% and .9% max relative error.
          xL = T0*(.245374+T0*(.61952+T0*(-.0848+T0*.221)))
          xS = T0*(.63275+T0*(-.98298+T0*.50498))+1.2199*log(1+T0)
          zlam = (xS - x)/(xS - xL)
500       return
          end
c-----------------------------------------------------------------
        subroutine ENTHALS(x,T,h)
c..........given x,T, find h(x,T) (cal/mol) for Solid alloy:
         omegaS = 1553.5373
         T0 = T * 1.e-3
c..........reference enthalpies of Solid A=Ge and B=Si :
         h0SA = -1600.675+5160.*T0+700.*T0*T0
         h0SB = -2063.69+5720.*T0+295.*T0*T0+99./T0
         xA = 1.-x
         h = xA*(h0SA + omegaS*x*x) + x*(h0SB + omegaS*xA*xA)
         return
          end
c-----------------------------------------------------------------
        subroutine ENTHALL(x,T,h)
c..........given x,T, find h(x,T) (cal/mol) for Liquid alloy :
          omegaL = 836.52
          T0 = T * 1.e-3
c............reference enthalpies of Liquid A=Ge and B=Si :
          h0LA = 6481.897 + 6600.* T0
          h0LB = 10258.635 + 6120. * T0
          xA = 1.-x
          h = xA*(h0LA + omegaL*x*x) + x*(h0LB +omegaL*xA*xA)
        return
          end
c-----------------------------------------------------------------
        subroutine ENTHALm(x,T,xL,xS,zlam,h)
c..............find h(x,T) (cal/mol) for mushy alloy :
          call ENTHALL(xL,T,hL)
          call ENTHALS(xS,T,hS)
          h = zlam*hL + (1.-zlam)*hS
        return
          end
c-----------------------------------------------------------------
```

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