Thermodynamic assessment of Binary systems

Tris(hydroxymethyl)aminomethane -Pentaglycerine (TRIS-PG) and 2-amino-2-methyl-1,3-propanediol-Pentaglycerine (AMPL-PG) Phase diagrams

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Abstract

Solid state phase change materials are considered as potential candidates for thermal energy storage. Among the solid-solid heat storage materials, the most promising heat storage materials are organic polyalcohol globular tetrahedral molecular crystals such as $(\text{CH}_3)\text{C}(\text{CH}_2\text{OH})_3$ for PG, $(\text{NH}_2)\text{C}(\text{CH}_2\text{OH})_3$ for TRIS, and $(\text{CH}_3)(\text{NH}_2)\text{C}(\text{CH}_2\text{OH})_2$ for AMPL, which store a large amount of thermal energy in their solid state high temperature phases with orientationally disorder crystal structure. In this study, we obtained the Gibbs energies of pure PG and pure TRIS derived utilizing the available experimental data including temperature-dependency of heat capacity, enthalpy, and transitions temperatures, as well as obtained *optimized* binary phase diagrams of TRIS-PG and AMPL-PG by CALPHAD calculations. The phase boundaries are verified by in-situ X-ray diffraction (XRD). Optimized database of these two binaries will allow exploration of ternary and higher order systems using CALPHAD methodology that will provide a wider selection of materials for practical thermal energy storage applications. Regular and sub-regular solution models are used for calculations in which the excess Gibbs energies are expressed by the Redlich-Kister-Muggianu polynomial. A set of self-consistent interaction parameters formulating the Gibbs energies of various phases in binary systems are obtained. The TRIS-PG binary phase diagram was calculated from room temperature to the liquid phase temperature, the modeled phase diagram and the experimental data from our work are in good agreement. We also used experimental data of TRIS-PG from the literature which shows a good agreement between the two data sets. Our optimized TRIS-PG phase diagrams show a wider solid-state two phase region, where there is de-mixing of phases, whereas the calculations from the literature show a very narrow region. We also present optimized AMPL-PG binary phase diagram using PARROT module in Thermal-Calc

software. The calculated phase diagrams for the two systems mentioned above are presented along with the experimental data.

I. Introduction

Thermal energy storage materials are gaining importance in environmental and ecological systems. Thermal energy can be stored as sensible and latent heat in materials in solid-liquid or solid-solid phase change materials; the stored thermal energy may be released later by cooling the material [1]. In addition, thermal energy storage materials can also be used in applications for waste heat recovery, solar energy utilization, energy saving in buildings, and electronic device management [2]. Phase change materials (PCMs) [3] have a great potential for thermal energy storage, absorbing/releasing heat during their phase transitions. PCMs are classified according to the phase transition involved (1) solid-solid phase transition, and (2) solid-liquid phase transition materials. In 1938, Timmermanns [4] proposed a special class of organic materials and classified them as globular molecules. This group of organic molecular crystals exhibit polymorphisms that are characterized by high enthalpies of solid-solid transitions and a low enthalpy of fusion. An important characteristic of these molecules is that they undergo reversible phase transition from a low temperature layered or chain structure (tetragonal, orthorhombic, monoclinic etc.) to a high temperature orientationally disordered phase such as face centered cubic (FCC) and body centered cubic (BCC). This high temperature phase is referred to as orientationally disordered crystal (ODIC) or plastic crystal phase. Alcohol or amine derivatives form these “Plastic Crystals,” such as Pentaglycerine (PG), $(\text{CH}_3)\text{C}(\text{CH}_2\text{OH})_3$, 2-hydroxymethyl-2 methyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol (AMPL), $(\text{NH}_2)(\text{CH}_3)\text{C}(\text{CH}_2\text{OH})_2$, and Tris(hydroxymethyl)aminomethane (TRIS), $(\text{NH}_2)\text{C}(\text{CH}_2\text{OH})_3$ etc.

Crystallographic and thermodynamic parameters of the pure polyalcohol and amines are already established in the literature [5-13]. The low temperature crystal structure of AMPL is reported by Rose et al. [5] as monoclinic with lattice parameters: $a=8.62 \text{ \AA}$, $b=11.00 \text{ \AA}$, $c=6.10 \text{ \AA}$, $\beta=93.32^\circ$, $V=580.3 \text{ \AA}^3$ at 293K ($Z=4$). The molecular structures of AMPL are shown in Figure 1. Chandra et al. [7] reported high temperature phase structure of AMPL as body centered cubic (BCC) with $a=6.78 \text{ \AA}$ above $\sim 365\text{K}$. Eilerman and Rudman [9-10] reported the low temperature structure of TRIS is orthorhombic $Pn2_1a$ (space group 33) with lattice parameters $a=8.844(1) \text{ \AA}$, $b=7.794(1) \text{ \AA}$, $c=8.795(1) \text{ \AA}$, $Z=4$. At low temperature, TRIS forms layered or chain structures where hydroxyl groups are connected by strong hydrogen bonds within each layer and amine groups are connected by relatively weak hydrogen bonds. The molecular structure of TRIS is also shown in Figure 1. Eilerman and Rudman [9-10] also reported the high temperature phase of TRIS as body centered

cubic (BCC), $Im\bar{3}m$, with $a=6.876(6)\text{\AA}$ at 423 K ($Z=2$). Low temperature phase of the PG was determined by Eilerman et al. [11] as tetragonal (space group I-4) with $a=6.054\text{\AA}$ and $c=8.866\text{\AA}$; three hydroxyl groups form the connection of strong hydrogen bonds in the layers of ordered crystal structure reported by Barrio et al. [12]. Doshi et al. [13] reported that the PG undergoes a solid state phase transition at 351.3 K to high temperature phase with an orientationally disordered face-centered cubic (FCC) with a lattice parameter, $a=8.86(5)\text{\AA}$ at 373 K.

Figure 1 Molecular structures of PG($C_5H_{12}O_3$), TRIS($C_4H_{11}NO_3$), and AMPL($C_4H_{11}NO_2$).

For practical applications, solid-state phase transition temperatures (T_{SSTR}) of pure materials range from 353 K (AMPL) to 407 K (TRIS); there are only a few materials with these characteristics. In order to increase the selection of these energy storage materials, we make polyalcohol and amine solid solutions that have different phase transition temperatures (T_{SSTR}) to suit a particular application [14]. To study the effect of solutions/mixtures of polyalcohol and amines on the solid-solid phase transitions, Barrio et al. [12] conducted experimental investigations on binary system such as TRIS-PG. Lopez et al. [15] carried out computational studies of molecular mixed crystals of TRIS-PG. However, there is a significant difference between Barrio's experimental results and Lopez's computational phase diagram about the low temperature phase regions for PG-rich solid solution and TRIS-rich solid solution. Salud et al. [16] established a comparative analysis of crystallography and thermodynamics of AMPL-PG. As part of our ongoing work on creating new binaries for thermal energy storage applications, Gantan [17] conducted the AMPL-PG system experiment work as a part of his M.S thesis. Salud et al. [16] performed further experimental studies on the AMPL-PG system including a calculated phase diagram, but there were slight differences between these two-phase diagrams of Gantan [17] and Salud et al. [16].

In this study, the optimized phase diagrams of TRIS-PG and AMPL-PG are determined, by using available experimental data from our work as well as the literature [12, 16, 17], which are remarkably important to understand the polymorphism in the binary systems, and further develop ternary or higher order systems to develop more materials for thermal energy storage.

II. Materials and Methods

2.1 Materials

Polycrystalline samples of PG (99%), TRIS (99.9%), and AMPL (99.9%) were procured from Sigma-Aldrich; The samples were heated in VWR KIMAX, Culture tubes (20 mmx125 mm) with sealable screw top. These samples were heated in air using a standard Bunsen burner, once the powders melted; we sealed the tube with the screw top so as to prevent any moisture back-streaming into the sample. The TRIS-PG, and AMPL-PG mixture binary samples were prepared at various compositions, and all compositions were reported as mole% in this paper. We followed a protocol in which the sample powders were premixed and melted in test tubes. Generally, the solidified melt does not give an equilibrium mixture of solid phases due to supercooling, and high temperature phases are retained at room temperature. To avoid this, we used strain induced transformation method in which equilibrium phases were attained. The methodology involves placing the melted and solidified binary mixtures in a freezer (~253 K) for 12 hours and then subjected them to a high strain in a small cylinder with a piston. This method worked well to obtain equilibrium crystal structures at room temperature.

2.2 X-Ray Diffraction analyses

In-situ x-ray diffraction studies were performed, using a θ - θ PANalytical X'Pert PRO diffractometer, to determine the lattice parameters by superimposing the lattice symmetry of the pure PG, TRIS, AMPL, and their binary solid solutions (TRIS-PG, and AMPL-PG). Powder samples of binary solid solutions were prepared by adding an internal standard silicon powder. A PANalytical x-ray diffractometer system was modified to accept sapphire capillaries as sample holders. This home-made device was fabricated using hot air blowing system incorporated with the diffractometer, and the temperature was maintained by using a Watlow temperature controller with a feedback to the hot air blower. A position sensitive detector, which is part of the PANalytical diffractometer, was used to capture the diffraction angles and intensities of the Bragg peaks. The diffraction scans were made using $\text{CuK}\alpha$ radiation, and the analyses were performed by using MDI Jade 6.5 software.

2.3 Computational Procedures

2.3.1 Thermodynamic properties of pure PG, TRIS, and AMPL

Experimental data, such as enthalpies and temperatures of phase transitions for pure PG, TRIS, and AMPL used for this calculation were taken from this work (listed in Table 1). The solid-solid and solid-liquid phase transition temperatures of pure PG reported from Murrill and Breed [14] were lower than our present work, but our values were close to those reported earlier [16, 18, 19]. The melting temperature of pure TRIS (~445 K) which was reported by previous literatures [12, 13, and 20] was close to the values we reported in this study. The solid-solid and solid-liquid phase transition temperatures of pure AMPL reported from Murrill and Breed [14] were close to our present work and also close to the values provided by Sigma-Aldrich. Phase transition temperature for pure AMPL reported in reference [7, 21-22] was higher than that reported in literature. Also, Zhang et al. [23], reported an additional first-order transition in AMPL determined by adiabatic calorimetry at 353.7K between the known monoclinic (low temperature phase) and the BCC (high temperature phase). Witusiewicz et al. [24] designated this phase as AMPD-II in his paper. Thermodynamic properties of pure PG, TRIS, and AMPL obtained in this work are shown in Table-1, as well as the data of AMPD-II obtained from the reference of Zhang et al. [23], and were used for calculations and optimization. The experimental heat capacity of PG was measured using DSC by Chandra et al. [25] in the temperature range of 305K-447.5K including above ambient solid-solid phase properties. The low temperature heat capacity of PG was obtained adiabatically by Keishi et al. [18] over temperatures ranging from 18.36K to 374.56K; the sub-ambient heat capacity of PG was also obtained adiabatically from our groups' unpublished work from 1.91K to 300.444K. The data from above experiments [18, 25, and our unpublished work] complement each other and are in good agreement in the mid-range where these data overlap with those of reference [18]. The heat capacity data of TRIS was obtained by using DSC from Chandra et al. [25] in the temperature range of 305K-447.5K, by using MDSC from Suresh et al. [26] over a temperature range of 193.5K-473.15K. Also, the experimental heat capacity of TRIS was obtained adiabatically by Arvidsson et al. [27] in the temperature range from 5K to 350K and Zhang et al. [28] in the temperature range from 294.4K to 450.64K. The heat capacity of TRIS from Suresh et al. [26] and Arvidsson et al. [27] complement each other and in the overlapped region has a good agreement. However, the data for pure TRIS from Chandra et al. [25] and Zhang et al. [28] are slightly scattered above ambient solid-solid phase transition temperature. In the optimization, the higher weight for heat capacity was assigned to the data from Keishi et al. [18], Chandra et al. [25], and our unpublished work (previous work) for PG as well as assigned to the data from Suresh et al. [26] and Arvidsson et al. [27] for TRIS due to better convergence of heat capacity. Thermodynamic description of AMPL with experimental heat capacity from Chandra et al. [25] and Zhang et al. [23] was performed by Witusiewicz et al. [24] by using CAPPHAD method.

Table 1 Lattice Symmetries, transition temperatures and thermal properties of PG, TRIS, and AMPL (bold letters were used for present calculation).

Compound	Low Temp. phases	T _{TR} (K)	ΔH _{TR} (KJ/mol)	ΔS _{TR} (KJ/mol*K)	High Temp. phases	T _F (K)	ΔH _F (KJ/mol)	ΔS _F (KJ/mol*K)	Refer.
PG	Tetragonal	356.6	19.06- 22.74	0.06	FCC	473.7	4.63- 4.84	0.01	[16]
		356.7	20.94	0.06		474.4	4.7	0.01	[19]
		357.5	19.9	0.06		474.1	4.7	0.01	In this study
		407.2	34.5	0.08		445.4	3.4	0.008	In this study
TRIS	Orthorhombic	407.3	32.9	0.08	BCC	446	3.0	0.007	[13]
		406.8	34.0	0.08		442.7	3.7	0.008	[12]
		353	23.3	0.07		385	3.0	0.008	[20]
AMPL	Monoclinic	353.4	24.9	0.07	BCC	384.7	3.3	0.008	In this study
		352.9	23.8	0.07		383.5	2.7	0.007	[24]
	AMPD_II	353.72	18.5	0.05		384.08	2.8	0.007	[23]

2.3.2 Binary Phase Diagram data

The TRIS-PG binary phase diagram was previously reported by Barrio et al. [12] and Lopez et al. [15]. Barrio et al. [12] proposed a TRIS-PG experimental phase diagram using DSC and X-ray diffraction with the first low temperature eutectoid invariant at 346.7K. Below 346.7 K, they reported two low temperature solid state phases between 2 and 92 %PG. Above this temperature, Barrio et al [12] reported a two phase region from 384.7 K to 431.6 K in the composition range of 45 to 68%PG. Lopez et al. [15] calculated TRIS-PG phase diagram in which the first low temperature eutectoid reaction was reported at 346.4 K. Below this temperature, their TRIS-PG, phase diagram showed a two O (Orthorhombic) and Q (Tetragonal) phase region from 0-100% PG. Both Lopez et al. [15] and Barrio et al. [12] reported a high temperature second eutectoid invariant at 385.7 K. The TRIS-PG phase diagrams of Lopez et al. [15], and Barrio et al. [12] showed the differences in the phase stability regions. Because of these uncertainties in the phase stability regions reported in the literatures, we re-assessed the TRIS-PG binary phase diagram in this present study using our experimental data and also some of the data from Barrio et al. [12] in order to obtain details of phase transformations to compile data for the calculation of ternary or higher systems.

We also found an AMPL-PG binary phase diagram in the literature, but we observed problems with the phase stabilities in the low and high temperature regions, especially in the PG rich regions; this phase diagram was reported by Salud et al. [16]. In the experimental AMPL-PG phase diagram of Salud et al. [16], a low temperature solid-state eutectoid was reported at 323K leading to M1 (Monoclinic)+Q (Tetragonal) region in the composition range of 9 to 92% PG. A second high temperature eutectoid was also reported at 330.2K leading to a Q(Tetragonal)+C_I(BCC) phase region in the composition range of 44 to 93% PG. They also reported a peritectic at 413.6 K. Salud et al. [16] also calculated the AMPL-PG phase diagram, and found three invariant temperatures that were 3-7 K higher than their experimental temperatures.

More recently, in our group, Gantan [17] determined an experimental AMPL-PG phase diagram using in-situ X-ray diffraction which showed that the PG-rich low temperature phase started from 82%PG to pure PG. In general, we found minor differences between Gantan [17] and Salud et al. [16] phase diagrams. But there was an issue with the stabilities in the PG rich region as compared to Gantan [17]. In this work, the AMPL-PG binary system has been recalculated using Gantan's [17] experimental data; we also used a part of the experimental data of Salud et al. [16].

2.3.3 Thermodynamic modeling

In this study, we focused on (1) the analytical description of the Gibbs energies of pure PG and pure TRIS derived by utilizing the available experimental data including temperatures, enthalpies at phase transitions, and dependent-temperature heat capacity; (2) optimization using regular and sub-regular solution models with CALPHAD methodology to obtain excess Gibbs energies of various phases. Thermodynamic evaluations of similar organic systems such as TRIS-AMPL [6], PE-AMPL [20], and AMPL-NPG [22] were performed using CALPHAD method. Unfortunately, in our previous work [6, 20, 22], the experimental heat capacity of various phases in pure material were extrapolated traditional (linear) manner [22], but if we use this linear extrapolation of heat capacities between the room temperature and the melting point, we obtain global features of the phases in this temperature range. However, at very high and very low temperature we have phase stability issues. For example, liquid phase appear below the room temperature and solid phases appear at very temperature, above the liquid phase. Note that the phase diagrams calculated using linear extrapolation of the heat capacity, between the room temperature and the melting points, of the materials are comparable with the phase diagrams obtained using non-linear extrapolation of heat capacity. In some cases we observed BCC and FCC phases at higher temperatures in the liquid phase region, or high temperature phases at very low temperatures, obviously not correct. Witusiewicz et al. [24] presented a method to establish these phase diagrams between close to zero K to higher than 1000K. They established heat capacities using Dinsdale [29] approach in which

sub-ambient heat capacity data is required. To address this we started making sub-ambient heat capacity measurements by adiabatic methods for several pure organic compounds, yet to be published. In corporation of these heat capacities has solved the problem of phase stability issues.

2.3.3.1 Pure substances

The thermodynamic properties of most of pure substances are described in SGTE-compilation by Dinsdale [29]. However, there is no available thermodynamic database to describe thermodynamic properties for pure PG and pure TRIS in the world. In the previous work [20, 30-32] from our group, the Gibbs energy in its standard element reference (SER) state was set to zero, and the heat capacity was extrapolated as straight lines in a limited range of temperature [22] that resulted in erroneous phase stability regions in the very low and very temperature ranges, for example, we observed a liquid phase below room temperature, and solid FCC or BCC phases well above the melting point of the material. However between the room temperature and the melting point of the material, the global features of the phase diagram were fine. In this study, the temperature dependence of the molar Gibbs energy referred to such standard state ($G.H^{SER} = {}^0G - H^{SER}$) and the heat capacity (C_p) of a phase is usually described as a power series in terms of temperature T in the form [29].

$$GH^{SER} = A + BT + CTLnT + \sum DT^n, \quad (\text{Eq. 1})$$

$$C_p = -C - \sum n(n-1)DT^{n-1} \quad (\text{Eq. 2})$$

where H^{SER} is the enthalpy of formation of a pure substance at 298.15K and 1 bar in its standard element reference (SER) state. First we determine coefficients C and D and then all the parameters A, B, C and D in the PARROT on the basis of available experimental data including temperature-dependency of heat capacity, temperatures, and enthalpies at phase transitions, and n represent a set of integers. The thermodynamic description of pure substances in this study is valid at sub-ambient temperatures and according to the third law of thermodynamics $C_p(0K) = 0$, the parameter C was set as zero.

2.3.3.2 Solution Phase

In this section, we will discuss the general concepts of our computational models by using a category “A” system which can be easily extended to a category “B” system. Table 2 shows list of symbols used to describe the various phases in TRIS-PG and AMPL-PG binary systems. If the standard reference state for each phase was determined of the pure components in that phase, then

Gibbs energy expressions of a solution phase ϕ ($\phi=\alpha, \beta, \delta, \gamma, \gamma', \eta, L$) can be represented as follows (Gibbs energy is calculated as J/mol of the formula unit throughout in this work):

$$G^\phi = x_A {}^\circ G_A^\phi + x_B {}^\circ G_B^\phi + RT[x_A \ln(x_A) + x_B \ln(x_B)] + G^{EX,\phi} \quad (\text{Eq. 3})$$

where x_A is the mole fraction of A, x_B is the mole fraction of B, and R is equal to 8.314 J/mol K. ${}^\circ G_A^\phi$ and ${}^\circ G_B^\phi$ are the Gibbs energies of pure components A and B in phase ϕ . $G^{EX,\phi}$ is the excess Gibbs energy. $G^{EX,\phi} = x_A x_B [L_0^\phi + L_1^\phi (x_A - x_B)]$, L_0^ϕ and L_1^ϕ are the excess Gibbs energy parameters which can be optimized by using the PARROT module of Thermo-Calc software and determined using the following form of a power series:

$$L_m^\phi = a + bT + cT \ln(T) + dT^2 + eT^{-1} + fT^3 + gT^7 + hT^{-9} \quad (\text{Eq. 4})$$

where a, b, c, d, e, f, g, and h are the excess Gibbs energy parameters. In most cases, only the first two terms of the above equation are used. If measured excess-heat-capacity data are available, the three term ($T \ln(T)$) will be added and used to represent a constant excess heat capacity[33].

Table 2 List of symbols denoting phases in TRIS-PG and AMPL-PG systems

Symbol	Phase
Liquid or L	Liquid
β	Low temperature PG Tetragonal (BCT) Phase
δ	Low temperature TRIS Orthorhombic Phase
α	Low temperature AMPL Monoclinic Phase
ζ	Low temperature AMPL AMPD_II Phase
γ	High temperature AMPL phase (BCC_A2)
γ'	High temperature PG FCC_A1 phase
η	High temperature TRIS phase (BCC_A2)

Reference state Gibbs energies are designated as ${}^\circ G_A^\alpha, {}^\circ G_B^\beta$ for the compounds rich in A (α phase) and B (β phase), respectively. Gibbs energies for all other stable and metastable phases of pure components are represented as changes from these reference states.

For example, the stable phases of “A” rich compounds are represented as α at low temperature and γ at high temperature, and for “B” as β at low temperature and γ' at high temperature. Gibbs energies of other phases in terms of these reference states can be represented as:

$${}^\circ G_A^\gamma - {}^\circ G_A^\alpha = \Delta {}^\circ G_A^{\alpha \rightarrow \gamma} \quad (\text{Gibbs energy change during } \alpha \rightarrow \gamma \text{ phase transition}) \quad (\text{Eq. 5})$$

$${}^\circ G_A^L - {}^\circ G_A^\alpha = \Delta {}^\circ G_A^{\alpha \rightarrow L} = \Delta {}^\circ G_A^{\alpha \rightarrow \gamma} + \Delta {}^\circ G_A^{\gamma \rightarrow L} \quad (\text{Overall Gibbs energy change } \alpha \rightarrow \text{Liq.}) \quad (\text{Eq. 6})$$

$$^{\circ}G_B^{\gamma'} - ^{\circ}G_B^{\beta} = \Delta^{\circ}G_B^{\beta \rightarrow \gamma'} \quad (\text{Gibbs energy of phase transformation of } \beta \rightarrow \gamma') \quad (\text{Eq. 7})$$

$$^{\circ}G_B^L - ^{\circ}G_B^{\beta} = \Delta^{\circ}G_B^{\beta \rightarrow L} = \Delta^{\circ}G_B^{\beta \rightarrow \gamma'} + \Delta^{\circ}G_B^{\gamma' \rightarrow L} \quad (\text{Overall Gibbs energy change } \beta \rightarrow \text{Liq.}) \quad (\text{Eq. 8})$$

The Gibbs energies of pure component stable phases $^{\circ}G_A^L$, $^{\circ}G_A^{\gamma}$, $^{\circ}G_B^L$, and $^{\circ}G_B^{\gamma'}$, were determined on the basis of experimental data including the heat capacity of pure substances, the enthalpies and transition temperatures available in the literatures. For example, the Gibbs energies of the stable phase of pure component “A”, in terms of enthalpies, entropies, and heat capacities are given in (Eq. 9) and (Eq. 10):

$$^{\circ}G_A^{\gamma} - ^{\circ}G_A^{\alpha} = \Delta^{\circ}G_A^{\alpha \rightarrow \gamma} = \Delta H_{TR} - T\Delta S_{TR} + \int_{T_{TR}}^T \Delta C_P^{\alpha \rightarrow \gamma} dT - T \int_{T_{TR}}^T \frac{\Delta C_P^{\alpha \rightarrow \gamma}}{T} dT \quad (\text{Eq. 9})$$

$$^{\circ}G_A^L - ^{\circ}G_A^{\alpha} = \Delta^{\circ}G_A^{\alpha \rightarrow \gamma} + \Delta^{\circ}G_A^{\gamma \rightarrow L} = \Delta H_{TR} - T\Delta S_{TR} + \int_{T_{TR}}^T \Delta C_P^{\alpha \rightarrow \gamma} dT - T \int_{T_{TR}}^T \frac{\Delta C_P^{\alpha \rightarrow \gamma}}{T} dT + \Delta H_F - T\Delta S_F + \int_{T_F}^T \Delta C_P^{\gamma \rightarrow L} dT - T \int_{T_F}^T \frac{\Delta C_P^{\gamma \rightarrow L}}{T} dT \quad (\text{Eq. 10})$$

Similar expressions extended from Eq. 9 and Eq. 10 can be obtained for Gibbs energies of stable γ' and liquid phases of “B”.

In this study, the metastable Gibbs energies $^{\circ}G_A^{\beta}$, $^{\circ}G_A^{\gamma'}$, $^{\circ}G_B^{\alpha}$, and $^{\circ}G_B^{\gamma}$ were estimated by using the Equal-Gibbs-Curve (EGC) proposed by Oonk[34]. For more details of this procedure refer to Lopez et al. [15] and Salud et al.[16] publications. In order to estimate $^{\circ}G_A^{\gamma'}$ and $^{\circ}G_B^{\gamma}$ in this A-B binary system, initially, we estimate the γ' and γ metastable melting points of the metastable phase A and B, respectively. For example, in a A-B binary system the narrow stable $[\gamma'+L]$ and $[\gamma+L]$ branches were extrapolated to $x=1$ and $x=0$ (x is the mole fraction of B in A-B system), respectively. Thus we obtained the melting points of metastable γ' -A and γ -B phases using EGC procedure. Thereafter, the melting enthalpy of metastable γ' -A and γ -B phases were obtained from the metastable melting point by using the entropy of melting to be the same as that of the stable form. Similar EGC procedures were used to estimate $^{\circ}G_A^{\beta}$ and $^{\circ}G_B^{\alpha}$ for metastable β -A and α -B phases for different A-B binary system.

III. Results and Discussion

3.1 X-ray Diffraction Results of TRIS-PG and AMPL-PG binary systems

Solid state phase transitions occurring in the TRIS (orthorhombic)-PG (body centered tetragonal) and AMPL (monoclinic)-PG systems were determined by using X-ray diffraction (XRD). First, we carried out ambient X-ray diffraction experiments on several samples of different compositions of the binary TRIS-PG solid solutions; results are shown in Figure 2. The low temperature TRIS rich region was labeled as Orthorhombic (TRIS-rich), whereas the PG rich low temperature region was

labeled as the Tetragonal (PG-rich). As the amount of PG increased, two-phase region for compositions form 2 to 95%PG. We show X-ray diffraction data for the solid solutions of 10, 50, and 80%PG in TRIS that show Bragg peaks that correspond to the Orthorhombic and Tetragonal phases. We added Si as a reference material to the samples. It should be noted that the phase diagram of Lopez et al. [15] showed no solid solution regions of the low temperature phases.

X-ray diffraction results of the AMPL-PG system are shown in Figure 3. XRD patterns taken at 313 K from various compositions of AMPL-PG binaries are shown in Figure 3. XRD data of the pure AMPL and PG are shown as reference. XRD data taken at 10%PG shows complete solubility of PG in AMPL, and we designate this as a Monoclinic phase. Between the compositions of 20-80%PG, we observed Bragg peaks of the Monoclinic+Tetragonal phases. The Tetragonal/Monoclinic+Tetragonal phase boundary is observed between 80 and 90%PG (Figure 3).

We also conducted in-situ X-ray diffraction experiments in the PG rich regions where there were uncertainties between Gantan [17] and Salud et al. [16] phase diagrams; the sample of 90%PG was heated from 298 K to 393 K in our X-ray diffractometer. XRD data were obtained at 6 different temperatures as shown in Figure 4. The Bragg peaks of single BCT tetragonal phase were observed at 298 K, 323 K and 333 K. At higher temperatures, between 363 K and 393 K, the single high temperature FCC_A1 phase Bragg peaks was observed.

3.2 CALPHAD Thermodynamic Calculations of the Phase Diagrams

The analytical description of the Gibbs energies of pure PG and TRIS was derived utilizing the data on temperature and enthalpy of transitions, and temperature dependencies of the heat capacity available in the literatures. Preliminary Gibbs energy calculations of TRIS-PG and AMPL-PG binary systems were calculated by assuming regular or sub-regular solution models which were used to evaluate the excess Gibbs energy parameters of the various phases. To determine the excess Gibbs energy parameters, thermodynamic optimization utilizing all available experimental data is needed [35]. The excess Gibbs energy parameters were obtained by using the PARROT module of the Thermo-Calc software [35-36]. The detail results of calculated TRIS-PG and AMPL-PG were summarized in the following sections.

Figure 3. Constant temperature XRD patterns taken at 313 K of various compositions of AMPL-PG binary system.

Figure 4. XRD patterns taken at various temperature of the 10AMPL-90PG sample.

3.3 TRIS-PG Binary Phase Diagram Calculations

The Gibbs energy parameters of pure PG listed in Table 3 were calculated by using the experimental data including heat capacity data from Keishi et al. [18], Chandra et al. [25], and our previous work as well as enthalpies and phase transition temperatures listed in Table 1. Fig.5(a) presents a comparison of calculated heat capacity data from thermodynamic description of Gibbs energy with experimental heat capacity of pure PG in this study. Fig.5 (b) shows the temperature variation of the Gibbs energy of various phases of pure PG relative to FCC_A1 phase. The Gibbs energy parameters of pure TRIS listed in Table 4 were assessed by utilizing experimental heat capacity from Suresh et al. [26] and Arvidsson et al. [27], as well as enthalpies and transition temperatures listed in Table 1. Fig.6 (a) exhibits calculated values of temperature dependency of heat capacity of pure TRIS from present description of Gibbs energy in a good agreement with

experimental heat capacity. Fig.6 (b) illustrates the temperature variation of the Gibbs energy of various phases of pure TRIS relative to BCC_A2 phase. Table 5 showed the transition temperatures and enthalpy changes for different phases of stable and metastable forms in TRIS-PG and AMPL-PG binary systems

Figure 5. (a) Heat capacity and (b) Gibbs energy of various phases of pure PG relative to FCC_A1 phase; points from experimental data [18, 25], and lines from present description.

Figure 6. (a) Heat capacity and (b) Gibbs energy of various phases of pure TRIS relative to BCC_A2 phase; points from experimental data [25-28], and lines from present description.

The TRIS-PG phase diagram was calculated and optimized using regular and sub-regular solution models with our experimental data as well as Barrio et al. [12]. The calculated TRIS-PG system resulted in a complex phase diagram as shown in Figure 7(a). The optimized excess Gibbs energy (G^{EX}) parameters for TRIS-PG binary system are listed at Table 6.

Low temperature Orthorhombic (TRIS-rich), Tetragonal (PG-rich), and Orthorhombic+Tetragonal two-phase regions are shown in our calculated TRIS-PG phase diagram which is matched to Barrio et al. [12] experimental phase diagram. Lopez et al.'s [15] calculated phase diagram did not show any solubility of TRIS in PG or vice-versa. (Figure 7(b)); they reported presence of mixture of pure phases of TRIS and PG in the low temperature regime. Based on the XRD results in the Figure 2 and calculated parameters, we show the single Orthorhombic and Tetragonal phase regions, and designated the low temperature two-phase region as Orthorhombic+Tetragonal region below ~349 K.

The high temperature phases start to appear above the first eutectoid (at 348.5K); these results are nearly the same as reported by Lopez et al. [15]. Above 348.5K, the low temperature phase Tetragonal transforms to high temperature phase FCC_A1, which coexists with the Orthorhombic phase up to 385 K. The first eutectoid, FCC_A1→Orthorhombic+Tetragonal, occurs at 348.5K (81%PG). Lopez et al. [15] and Barrio et al. [12] reported nearly similar eutectoid temperatures. There are large BCC_A2 and FCC_A1 phase regions and the BCC_A2+ FCC_A1 region are found between 44%-67%PG. These two high temperature BCC_A2 and FCC_A1 phases store different amount of energy. The second eutectoid is observed at 385.8 K, where BCC_A2→ Orthorhombic+ FCC_A1 at 44%PG. Note that the two-phase BCC_A2+FCC_A1 region calculated by Lopez et al. [15] is very narrow as compared to ours.

A comparison of the calculated and the experimental invariant equilibrium for TRIS-PG binary system are shown in Table 7. The liquid phase begins to appear above 427.5 K. A eutectic reaction ($L \rightarrow \text{BCC_A2} + \text{FCC_A1}$) is observed at this temperature and the composition of 46% PG. The corresponding eutectic temperatures and compositions observed by Barrio et al. [12] and Lopez et al. [15] are 430.4K (38 %PG) and 432.5 K (30%PG), respectively.

Table 3 Expression for Gibbs energies of pure PG, stable Phases (β =Tetragonal and γ' = FCC_A1 Structures).
(in J/mol PG)

Phase/equation	Temperature range(K)
Tetragonal: ${}^o G_{PG}^{\beta} = -15630.66+55.7T-.45T^2+3.39E-04T^3-3.01E-07T^4$	10≤T≤600
FCC_A1: ${}^o G_{TRIS}^{\gamma'} = +8329.32-.34T^2-2.45E-04T^3+2.29E-07T^4$	10≤T≤474.1
${}^o G_{TRIS}^{\gamma'} = +25899.38-59.86T-.45T^2+3.39E-04T^3-3.01E-07T^4$	474.1≤T≤600
Liquid: ${}^o G_{PG}^L = +13043.32-9.94T-.34T^2-2.45E-04T^3+2.29E-07T^4$	10≤T≤474.1
${}^o G_{PG}^L = +30613.38-69.79T-.45T^2+3.39E-04T^3-3.01E-07T^4$	474.1≤T≤600

Table 4 Expression of Gibbs energies of pure TRIS (δ = orthorhombic and η = BCC_A2 Structures).
(in J/mol TRIS)

Phase/equation	Temperature range(K)
Orthorhombic: ${}^o G_{TRIS}^{\delta} = -9096.72+18.65T-.37T^2+1.91E-04T^3-1.56E-07T^4$	10≤T≤445.4
${}^o G_{TRIS}^{\delta} = +76898.99-15.05T-1.06T^2+.0011T^3-6.47E-07T^4$	445.4≤T≤600
BCC_A2: ${}^o G_{TRIS}^{\eta} = +5412.81-.28T^2-2.54E-04T^3+1.52E-07T^4$	10≤T≤445.4
${}^o G_{TRIS}^{\eta} = +54631.46+257.25T-1.82T^2+.0018T^3-8.55E-07T^4$	445.4≤T≤600
Liquid: ${}^o G_{TRIS}^L = +8779.81-7.56T-.285T^2-2.54E-04T^3+1.52E-07T^4$	10≤T≤445.4
${}^o G_{TRIS}^L = +57998.46+249.69T-1.82T^2+.0018T^3-8.55E-07T^4$	445.4≤T≤600

Table 5 Transition temperatures and Enthalpies of various phases of Stable (s) and Metastable (m) forms in binary TRIS-PG and AMPL-PG systems. (Bold letters were used for present calculation)

Phase		(1)TRIS-(2)PG	(1)AMPL-(2)PG
BCC	T ₁ (K)	442.7(s) ^a	384.7(s) ^b
		445.4(s)^c	384.7(s)^c
	T ₂ (K)	465.0(m) ^a	465.0(m) ^b
		464.3(m)^c	464.3(m)^c
	ΔH_1 (J/mol)	3100(s) ^a	2700(s) ^b
		3367(s)^c	2981(s)^c
	ΔH_2 (J/mol)	5022(m) ^a	4650(m) ^b
		4623.5(m)^c	4623.5(m)^c
FCC	T ₁ (K)	432.4(m)^a	363.5(m)^b
	T ₂ (K)	471.7(s) ^a	473.7(s) ^b
		474.1(s)^c	474.1(s)^c
	ΔH_1 (J/mol)	3028(m) ^a	2552(m) ^b
		3268.5(m)^c	2631.0(s)^c
	ΔH_2 (J/mol)	5100(s) ^a	4737(s) ^b
		4714(s)^c	4714(s)^c
TETRAGONAL	T ₁ (K)	225.0(m)^a	348.3(m)^c
	T ₂ (K)	357.5(s)^c	357.5(s)^c
	ΔH_1 (J/mol)	18833(m) ^a	1651.8(m)^c
		4195.1(m)^c	
	ΔH_2 (J/mol)	19936(s)^c	19936(s)^c
ORTHORHOMBIC	T ₁ (K)	407.2(s)^c	
	T ₂ (K)	349.2(m)^c	
	ΔH_1 (J/mol)	34531(s)^c	
	ΔH_2 (J/mol)	19473.1(m)^c	
MONOCLINIC	T ₁ (K)		353.4(s)^c
	T ₂ (K)		344.9(m)^c
	ΔH_1 (J/mol)		24902(s)^c
	ΔH_2 (J/mol)		19232.2(m)^c

Note: superscript a=data from Lopez et al. [15], b=data from Salud et al. [16], c=data from this study.

Table 6. Summary of thermodynamic parameters of the solution phases in the TRIS-PG system (J/ mol formula unit)

Phase	Parameters
Body Centered Tetragonal (BCT)	${}^\circ L_{TRIS,PG}^{Tetragonal} = 2606.99-22.05T$
	${}^\circ G_{TRIS}^{Tetragonal} = GH_{TRIS}^{SER} + 10608.9$ (metastable)
Orthorhombic	${}^\circ L_{TRIS,PG}^{Orthorhombic} = 1834.06+24.18T$
	${}^\circ G_{PG}^{Orthorhombic} = GH_{PG}^{SER} + 948.8$ (metastable)
FCC _A1	${}^\circ L_{TRIS,PG}^{FCC(A1)} = 8213.87-22.27T$
	${}^1 L_{TRIS,PG}^{FCC(A1)} = 3098.21-20.59T$
	${}^2 L_{TRIS,PG}^{FCC(A1)} = -2096.48$
	${}^\circ G_{TRIS}^{FCC(A1)} = {}^\circ G_{TRIS}^{BCC_A2} + 98.5$ (metastable)
BCC_A2	${}^\circ L_{TRIS,PG}^{BCC(A2)} = 4357.79-12.48T$
	${}^1 L_{TRIS,PG}^{BCC(A2)} = 12614.55-32.66T$
	${}^2 L_{TRIS,PG}^{BCC(A2)} = -648.59$
	${}^\circ G_{PG}^{BCC(A2)} = {}^\circ G_{PG}^{FCC_A1} + 90.5$ (metastable)

Liquid	$\circ L_{TRIS,PG}^{Liquid}=38974.64-95.98T$			
	$\circ L_{TRIS,PG}^{Liquid}=-2213.72-3.6T$			

Table 7. Comparison of calculated and experimental invariant equilibrium for TRIS-PG binary system.

Invariant equilibria		X _{PG} (Mole of Fraction of PG)			Temperature(K)
		Orthorhombic	FCC_A1	Tetragonal	
Orth. +BCT → FCC_A1 (Eutectoid 1)	(C)	0.00	0.82	1.00	346.4 [15]
	(E)	0.02	0.82	0.92	346.7 [12]
	(C)	0.02	0.80	0.91	348.5 [This study]
		Orthorhombic	BCC_A2	FCC_A1	
Ortho.+FCC_A1→BCC_A2 (Eutectoid 2)	(C)	0.00	0.44	0.46	384.9 [15]
	(E)	0.02	0.45	0.68	385.7 [12]
	(C)	0.01	0.41	0.61	385.8 [This study]
		BCC_A2	L	FCC_A1	
BCC_A2+ FCC(A1)→L (Eutectic)	(C)	0.29	0.30	0.32	432.5 [15]
	(E)	0.35	0.38	0.43	430.4 [12]
	(C)	0.38	0.45	0.54	430.4 [This study]

E: Experiment, C: Calculation.

Figure 7. Calculated TRIS-PG phase diagram from this study.

3.4 Calculation of the AMPL-PG Binary Phase Diagram

The calculated Gibbs energy equations of pure AMPL were taken from Witusiewicz et al. [24]. The AMPL-PG phase diagram was calculated by using the same thermodynamic property procedure as for TRIS-PG system. The solution phases of the AMPL-PG binary system with experimental data from Gantan [17] and part of experimental data from Salud et al. [16] were modeled using regular and sub-regular solutions, and the phase diagram of AMPL-PG is shown in Figure 8(a). For comparison, we show the Salud et al. [16] phase diagram in Figure 8(b). The optimized excess Gibbs energy (G^{EX}) parameters obtained for the AMPL-PG system are listed at Table 8.

To establish accurate assessment, we focused on the differences in the calculations reported in the Salud et al. [16] that did not match our calculated data. The maximum composition of Tetragonal phase is up to 83%PG in our calculated phase diagram, as compare to the reported value of 92%PG in Salud et al. [16]. We performed high temperature X-ray diffraction results shown earlier on several compositions in this system allowed establishing of the Tetragonal/Monoclinic+Tetragonal phase boundary between 80%PG and 90%PG. We then established the phase boundary of the PG rich region using XRD analyses and showed that there is a single Tetragonal phase region up to 333 K at 90%PG (Figure 4). Table 9 shows comparison of the thermodynamic parameters of our data as compared to that in the literature [16]. Another difference between our calculated phase diagram and Salud et al. [16] is the eutectoid (BCC_A2→Monoclinic+Tetragonal) temperature. The eutectoid (BCC_A2→Monoclinic+Tetragonal) temperature is 323.5 K which is comparable with Salud et al.'s [16] experimental result as 323 K. However, Salud et al. [16] reported their calculated eutectoid (BCC_A2→Monoclinic+Tetragonal) temperature as 330 K which is ~7K higher than our calculated value. In summary, two eutectoids and one peritectic reaction were observed in the AMPL-PG binary phase diagram.

Table 8. Summary of thermodynamic parameters of the solution phases in the AMPL-PG system (J/mol formula unit)

Phase	Parameters
Body Centered Tetragonal (BCT)	${}^{\circ}L_{\text{AMPL,PG}}^{\text{Tetragonal}} = 8252.22 - 5.49T$
	${}^1L_{\text{AMPL,PG}}^{\text{Tetragonal}} = 2037.20$
	${}^{\circ}G_{\text{AMPL}}^{\text{Tetragonal}} = GH_{\text{AMPL}}^{\text{SER}} + 497.1$
Monoclinic	${}^{\circ}L_{\text{AMPL,PG}}^{\text{Monoclinic}} = 2596.68 + 6.63T$
	${}^1L_{\text{AMPL,PG}}^{\text{Monoclinic}} = 1995.30$
	${}^{\circ}G_{\text{PG}}^{\text{Orthorhombic}} = GH_{\text{PG}}^{\text{SER}} + 1389.6$
AMPD-II	${}^{\circ}G_{\text{PG}}^{\text{AMPD-II}} = GH_{\text{PG}}^{\text{SER}} + 4500$

FCC_A1	${}^{\circ}L_{AMPL,PG}^{FCC_A1} = -22488.94 + 58.58T$
	${}^1L_{AMPL,PG}^{FCC_A1} = 18842.71 - 48.14T$
	${}^{\circ}G_{AMPL}^{FCC_A1} = {}^{\circ}G_{AMPL}^{BCC_A2} + 151.9$
BCC_A2	${}^{\circ}L_{AMPL,PG}^{BCC(A2)} = -22635.70 + 59.28T$
	${}^1L_{AMPL,PG}^{BCC(A2)} = 2944.12 - 12.56T$
	${}^{\circ}G_{PG}^{BCC(A2)} = {}^{\circ}G_{PG}^{FCC_A1} + 90.5$
Liquid	${}^{\circ}L_{AMPL,PG}^{Liquid} = 1696.41$
	${}^1L_{AMPL,PG}^{Liquid} = -3511.68$

Table 9. Comparison of calculated and experimental invariant equilibria for AMPL-PG binary system.

Invariant equilibria		X _{AMPL} (Mole of Fraction of PG)			Temperature(K)
		BCT	BCC_A2	Monoclinic	
Mono.+ Tetra.→BCC_A2 (Eutectoid 1)	(C)	0.92	0.47	0.09	330.0 [16]
	(E)	0.92	0.43	0.09	323 [16]
	(C)	0.83	0.38	0.07	324.5 [This Study]
		Tetragonal	FCC_A1	BCC_A2	
Tetra.+ BCC_A2→FCC_A1 (Eutectoid 2)	(C)	0.96	0.54	0.51	333.5 [16]
	(E)	0.93	0.53	0.44	330.2 [16]
	(C)	0.88	0.56	0.44	333.0 [This Study]
		FCC_A1	BCC_A2	L	
L+ FCC_A1→ BCC_A2 (Peritectic)	(C)	0.56	0.53	0.48	418.4 [16]
	(E)	0.57	0.47	0.40	413.6 [16]
	(C)	0.54	0.46	0.37	413.5 [This study]

E: Experiment, C: Calculation.

Figure 8. Calculated AMPL-PG phase diagram from this study

IV. Conclusions

Gibbs energies of pure PG and pure TRIS were derived from available experimental data including temperature dependent heat capacity, enthalpy, and transformation temperatures that allowed calculation of phase diagrams from very low to very high temperature using heat capacity data in different ranges of temperatures. The assessment of the TRIS-PG and AMPL-PG binary phase diagrams with available heat capacities of pure compounds, and x-ray diffraction data allowed calculation of consistent phase diagrams of AMPL-PG, TRIS-PG phase diagrams that were optimized. Redlich-Kister-Muggianu polynomial and a set of self-consistent interaction parameters formulating the Gibbs Energies of various phases in binary systems were also obtained. In the case of TRIS-PG system (one eutectic and two eutectoids) the low temperature orthorhombic (δ -phase) and tetragonal (β -phase) were optimized using regular solution model. A sub-regular solution model for the high temperature, η phase-BCC_A2, γ' phase-FCC_A1 and Liquid phases. We used

the similar models to calculate the AMPL-PG system and found one peritectic and two eutectoid reactions. The main differences between our TRIS-PG and literature Lopez et al. [15] and Barrio et al. [12] are in the high temperature η or γ' regions. In the case of AMPL-PG system, the differences between our phase diagram and that of Salud et al. [16] are in the PG rich low temperature (β) region. Our new experimental data resolved the discrepancies in the phase diagrams reported in the literature. As suggested by Witusiewicz et al. [24], heat capacity extrapolation to zero K and to high temperatures above melting points of pure components is necessary to obtain accurate global features of the phase diagrams.

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