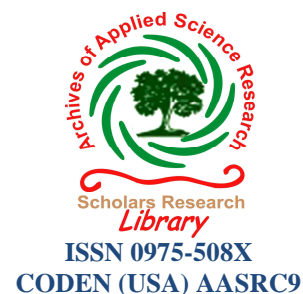




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Excess thermo functions Harbinger molecular interactions essence in binary condensed eutectic phases

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ABSTRACT

This investigation attributes the physical significance of the excess thermodynamic functions to their aesthetic ability in the domain of thermofunctions. Excess functions are discovered superior particularly in revealing the molecular interactions of binary condensed interphase molecules, since they provide the quantitative idea of deviations occurring in the experimental observations while exploring the solidus-liquidus phase equilibrium curves of binary transparent and opaque eutectic systems. These functions not only explain the miscibility criteria but also their physical behaviour at the condensed eutectic composition in view of Planck's theoretical concept of temperature independent entropy resulting in from the Weibull distribution of interphase molecules ensuring the complete stability of binary system at this very composition. The concept implicitly discusses the descending and ascending order in values of excess Gibbs free energy (G^E) and excess entropy (S^E) of mixing along either side of the solidus-liquidus equilibrium curve furnishing the eutectic composition accomplished with G^E minimum and S^E maximum followed by excess enthalpy of mixing, H^E . Moreover, excess functions are found capable of providing an alternative theoretical procedure to study the phase equilibria particularly of binary eutectic systems disseminating their physical understanding comprehensively. Guggenheim lattice theory offers supporting evidence to the aesthetic ability of excess functions harbinger the existence of molecular interactions in the binary condensed eutectic systems.

INTRODUCTION

The field of phase equilibria in materials science has become extensive and a number of review papers have appeared in the literature[1-6] but the nature and liquidus structure of eutectic phenomenon remain in quest. With a view to ascertain the structural behaviour of eutectic phenomenon in the phase equilibria, the excess thermodynamic functions are considered to be the best tool to reveal the molecular interactions between the binary condensed interphase molecules obtained by gradual mixing of one material with the other capable of forming eutectic mixture, i.e., both the materials must have different space groups in the solid state[7]. Thermodynamics restricts the number of experiments to define the state of a system[8-10] particularly when the experimentation times are quite long or equipment is expensive or not possible to design. Since no conceptual or theoretical framework is available in the literature for understanding the changes in the thermodynamic functions, namely, free energy, entropy, enthalpy, chemical potential, and specific changes in atomic or crystal structure, the excess functions simply account for changes in these functions that accompany the formation of nonideal solution models. Consequently, in the absence of accounting the crystal structure, the excess functions computed from the lone enthalpy of fusion data of the constituent phases[11-13] are enable to provide quantitative idea about the nature of molecular interactions which occur on the formation of such solution including the non-isostructural solutions on the orthoenstatite-diopside solvus[14-15]. The derivation of Nernst distribution law using excess thermodynamic functions is based on the conventions of classical thermodynamics[16]. The excess functions also find their applications in the

development of statistical theories based on fluid models, and play vital role in the formulation of an asymmetric solution model for multicomponent phase calculations[17,18].

The present work is carried out with the objective to explore three physical aspects, which are to (a) ascertain the structural behaviour of binary metallic eutectic systems, namely, Cd-Bi; Sn-Cd and Sn-Pb in view of facilitating their comparison with their transparent analogs, viz., naphthalene-*o*-nitrophenol; diphenylamine- α -naphthol and benzil-diphenyl, that certainly interprets the relative physical liquidus structures of opaque and transparent eutectic composites to the logical conclusion; (b) obtain quantitative idea of molecular interactions and (c) combine this experimental approach with standard equations to predict alternate procedure of binary phase diagram.

MATERIALS AND METHODS

2.1. materials and their purification

Homogeneous materials, diphenylamine (Merck, AR, mp 326.20K, $\Delta_f H = 18.50 \text{ kJmol}^{-1}$); *o*-nitrophenol (Merck, AR, mp 317.80K, $\Delta_f H = 17.70 \text{ kJmol}^{-1}$); benzil (BDH, AR., mp 367.90K, $\Delta_f H = 23.50 \text{ kJmol}^{-1}$); α -naphthol (Merck, AR, mp 368 K, $\Delta_f H = 23.10 \text{ kJmol}^{-1}$), diphenyl (BDH, AR., mp 341.90K, $\Delta_f H = 18.57 \text{ kJmol}^{-1}$), were used as supplied, while naphthalene (BDH, mp 353.30K, $\Delta_f H = 19.01 \text{ kJmol}^{-1}$) was purified by sublimation method. The melting temperatures of the aforementioned materials were determined by thaw-melt technique and are found on the order comparable to the literature values[19,20]. The metals, lead (The BDH, AR, mp 602 K, $\Delta_f H = 4.77 \text{ kJmol}^{-1}$), bismuth (Merck, AR, mp 545.70K, $\Delta_f H = 11.138 \text{ kJmol}^{-1}$), tin (Alpha Aesar, AR, mp 505K, $\Delta_f H = 7.15 \text{ kJmol}^{-1}$) and cadmium (Merck, AR, mp 596.50K, $\Delta_f H = 6.20 \text{ kJmol}^{-1}$), were also used as such, and their melting temperatures obtained by thermal analysis are found approaching the literature attributions[19,20]. The enthalpies of fusion of the homogeneous materials were vouched at their respective melting temperatures by thermal analysis, which are in good agreement with the reported values[19,20].

2.2. diagrams of state

The variable compositional mixtures covering the entire molfraction composition range of the experimental systems were prepared in pyrex tubes of nearly the same dimensions. The experimental pyrex tubes were sealed under vacuum to prevent the evaporation of the tubes' content and the homogeneity of the mixtures was attained by heat – chill method. The diagrams of state for binary naphthalene-*o*-nitrophenol, diphenylamine- α -naphthol and benzil-diphenyl eutectic systems were studied by determining solidus-liquidus temperatures over their respective entire molfraction composition range by thaw-melt technique, whereas the melting and liquidus temperatures of Cd-Bi, Sn-Cd and Sn-Pb eutectic systems were likewise obtained by thermal analysis.

RESULTS

The experimental observation comprising of melting temperatures and enthalpies of fusion of the constituent materials are provided in Table 1. Tables 2-7 respectively, record the solidus-liquidus equilibrium data of binary naphthalene-*o*-nitrophenol, diphenylamine- α -naphthol, benzil-diphenyl, cadmium-bismuth (Cd-Bi), tin-lead (Sn-Pb) and tin-cadmium (Sn-Cd), eutectic systems. Likewise, the solidus-liquidus equilibrium curves drawn in Figs.1-6, respectively represent the phase equilibrium data of the aforementioned binary eutectic systems.

Table 1: Melting temperatures and enthalpies of fusion of homogenous materials

Material	Melting temperature (K)		Enthalpy of fusion (kJ mol^{-1})	
	Experimental value	Literature value ⁸	Experimental value	Literature value ⁸
Naphthalene	353.50	353.30	19.10	19.01
<i>o</i> -Nitrophenol	318.50	317.80	19.25	17.70
α -Naphthol	368.00	368.00	23.32	23.10
Diphenylamine	326.50	326.20	18.60	18.50
Benzil	368.00	367.90	23.20	23.50
Diphenyl	343.20	341.90	18.58	18.57
Cadmium	596.00	596.50	6.19	6.205
Tin	509.00	510.00	7.00	7.15
Bismuth	545.00	545.70	11.20	11.138
Lead	602.50	602.00	4.55	4.77

Table 2: Solidus-liquidus equilibrium data for naphthalene (1)–o-nitrophenol (2) eutectic system

Molfraction of component (1)	Solidus temperature T_s (K)	Liquidus temperature T_m (K)	Ideal temperature T_{id} (K)
0.0000		318.50	
0.1002	303.50	315.50	314.60
0.2003	303.50	311.50	309.60
0.3003	303.50	304.50	304.00
0.3250(e*)	303.50	303.50	304.90
0.4002	303.50	311.50	310.20
0.5001	303.50	321.50	319.50
0.5999	303.50	330.50	328.00
0.7002	303.50	336.50	335.20
0.8001	303.50	343.00	341.50
0.9003	303.50	349.00	348.10
1.0000		353.00	

Table 3: Solidus-liquidus equilibrium data for diphenylamine(1)– α -naphthol (2) eutectic system

Molfraction of component (1)	Solidus temperature T_s (K)	Liquidus temperature T_m (K)	Ideal temperature T_{id} (K)
0.0000		368.00	
0.1002	317.50	362.50	363.00
0.2003	317.50	355.50	357.60
0.3003	317.50	349.50	351.70
0.4002	317.50	341.50	345.00
0.5001	317.50	334.50	337.50
0.5999	317.50	325.50	326.70
0.7002	317.50	315.50	318.10
0.7600(e*)	317.50	311.50	311.90
0.7999	317.50	314.50	316.90
0.8999	317.50	321.50	322.50
1.0000		327.00	

Table 4: Solidus-liquidus equilibrium data for benzil (1)–diphenyl (2) eutectic system

Molfraction of component (1)	Solidus temperature T_s (K)	Liquidus temperature T_m (K)	Ideal temperature T_{id} (K)
0.0000		343.00	
0.1002	321.50	336.50	339.70
0.2004	321.50	331.00	333.90
0.3003	321.50	326.00	327.00
0.3600(e*)	321.50	322.00	322.80
0.4001	321.50	330.00	330.20
0.5005	321.50	335.50	339.50
0.6001	321.50	344.50	347.00
0.7008	321.50	352.50	354.00
0.8003	321.50	356.00	360.10
0.9001	321.50	362.50	365.20
1.0000		368.00	365.20

Table 5: Solidus-liquidus equilibrium data for cadmium (1)–bismuth (2) eutectic system

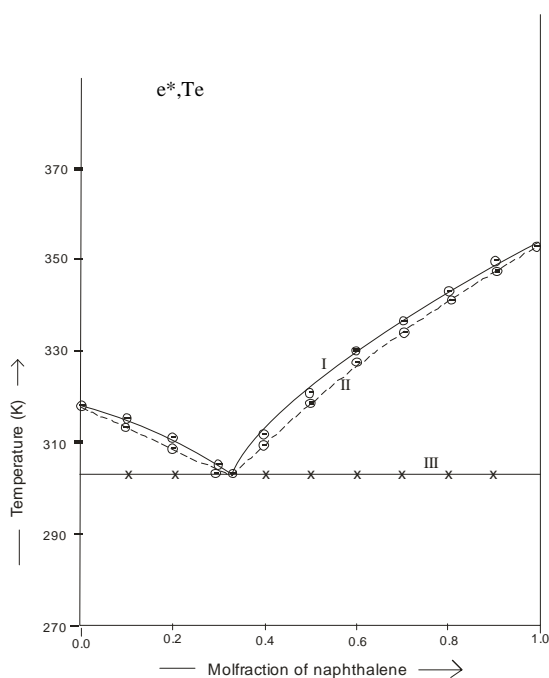
Molfraction of component (1)	Solidus temperature T_s (K)	Liquidus temperature T_m (K)	Ideal temperature T_{id} (K)
0.0000		545.00	
0.1710	417.00	503.00	506.00
0.3090	417.00	478.00	474.02
0.4400	417.00	443.00	441.23
0.5050(e*)	417.00	417.00	423.90
0.6560	417.00	466.50	446.00
0.7360	417.00	498.50	481.00
0.8150	417.00	530.00	521.80
0.8870	417.00	553.00	548.30
0.9520	417.00	573.00	574.00
1.0000		590.00	591.00

Table 6: Solidus-liquidus equilibrium data for tin (1)–cadmium (2) eutectic system

Mol fraction of component (1)	Solidus temperature T_s (K)	Liquidus temperature T_m (K)	Ideal temperature T_{id} (K)
0.0000	---	596.00	---
0.1002	449.00	567.00	554.00
0.2003	449.00	535.00	520.00
0.3003	449.00	509.00	490.00
0.4002	449.00	483.00	460.00
0.5001	449.00	468.00	440.00
0.5999	449.00	455.00	430.00
0.7003 (e^*)	449.00	449.00	425.00
0.8001	449.00	465.00	453.00
0.9003	449.00	490.00	485.00
1.0000	---	509.00	----

Table 7: Solidus-liquidus equilibrium data for tin (1) – lead (2) eutectic system

Mol fraction of component (1)	Solidus temperature T_s (K)	Liquidus temperature T_m (K)	Ideal temperature T_{id} (K)
0.0		602.00	
0.1	367.00	547.00	542.00
0.2	367.00	493.00	488.00
0.3	367.00	443.00	438.00
0.4	367.00	399.00	392.00
0.5 (e^*)	367.00	367.00	361.00
0.6	367.00	397.00	391.00
0.7	367.00	427.00	421.00
0.8	367.00	457.00	450.00
0.9	367.00	486.00	480.00
1.0	367.00	510.00	542.00

**Fig. 1 . Diagram of state of naphthalene–o-nitrophenol system**

Liquids temperatures curve; Ideal temperatures curve; Solidus temperatures; e^* : eutectic composition; T_e : eutectic temperature

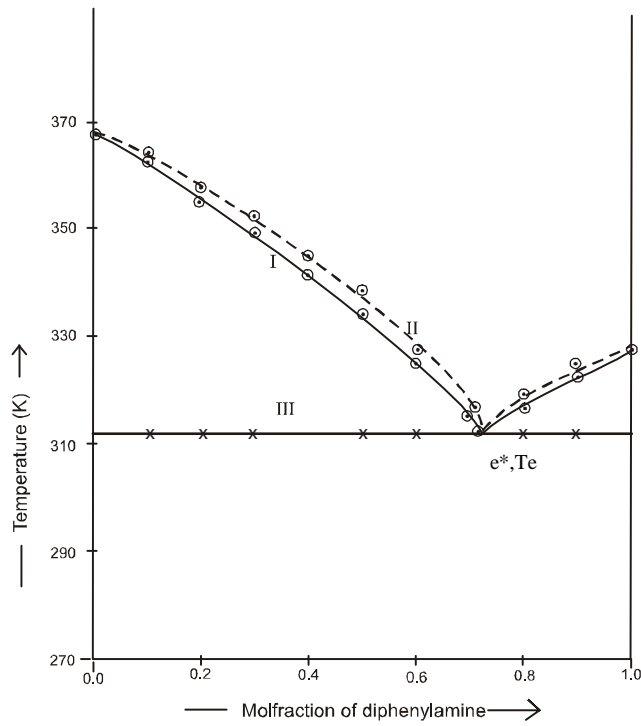


Fig. 2. Diagram of state for diphenylamine- α -naphthol system

Liquidus temperatures curve; Ideal temperatures curve; Solidus temperatures; e^ : eutectic composition; T_e : eutectic temperature*

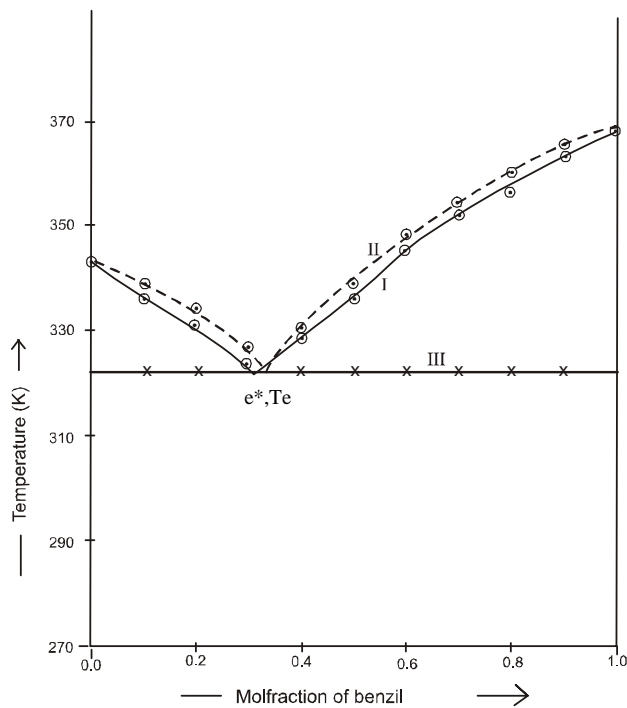


Fig. 3. Diagram of state for benzil-diphenyl system

Liquidus temperatures curve; Ideal temperatures curve; Solidus temperatures; e^ : eutectic composition; T_e : eutectic temperature*

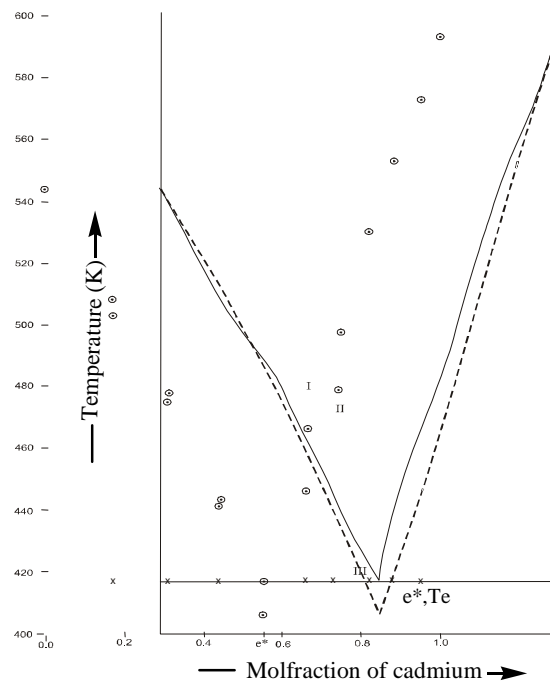


Fig. 4 . Diagram of state of Cd–Bi eutectic system

Liquidus temperatures curve; Ideal temperatures curve; Solidus temperature; e: eutectic composition; Te: eutectic temperature*

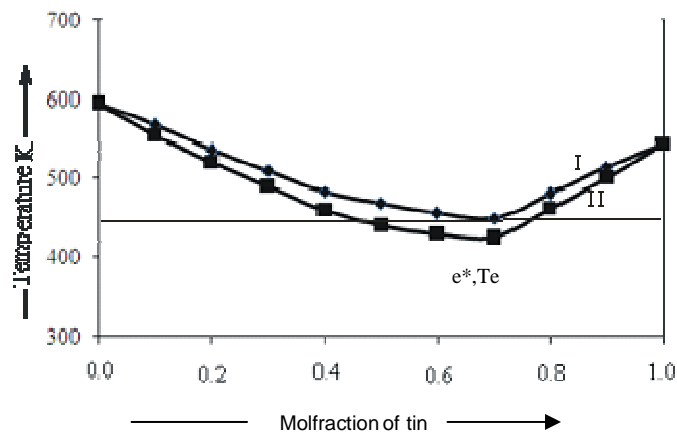


Fig. 5 . Diagram of state of Sn–Cd eutectic system

Liquidus temperatures curve; Ideal temperatures curve; Solidus temperature; e: eutectic composition; Te: eutectic temperature*

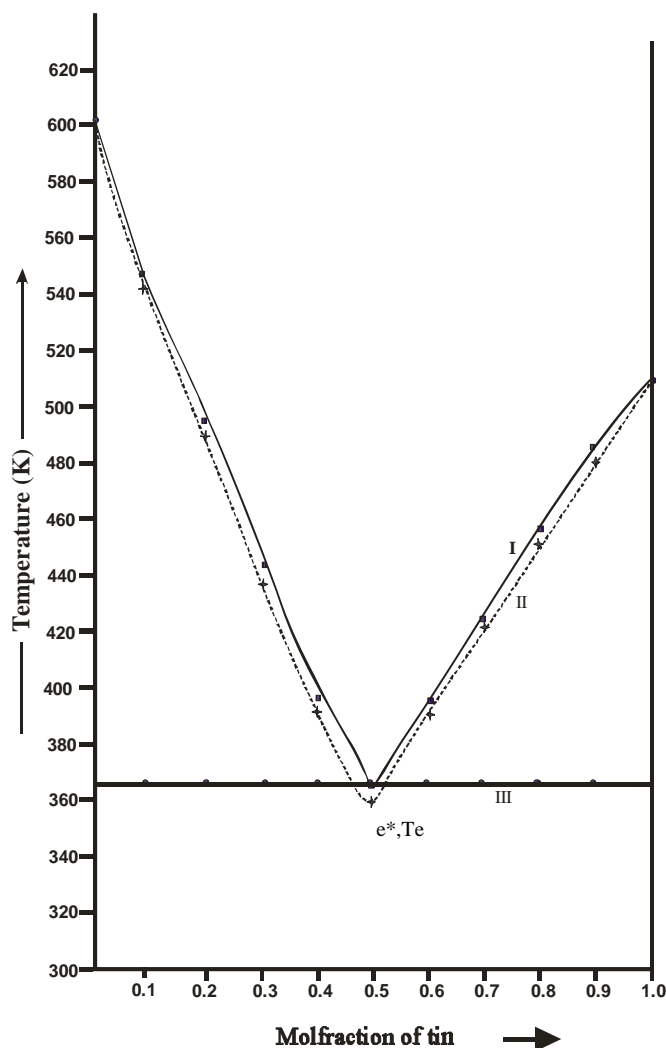


Fig.6. Diagram of state of Sn-Pb eutectic system

Liquidus temperatures curve; Ideal temperatures curve; Solidus temperature; e^* : eutectic composition; T_e : eutectic temperature

4. Theory

The important thermodynamic properties of any binary eutectic system can be extracted from the thermodynamic analysis of solidus-liquidus equilibrium data of that system in the condensed phase. In the present investigation, it is initially attained that each of the aforementioned experimental system is nonideal and the deviation from its ideal regions was ascertained by computing the activity coefficients of the eutectic phases i ($=1,2$), depending upon their richness in the pre- and post- binary mixtures vis-a-vis eutectic mixtures, at respective liquidus temperatures, T by the following equation [12,21]:

$$-\ln x_i^\ell \gamma_i^\ell = \frac{\Delta_f H_i^0}{R} \left[\frac{1}{T} - \frac{1}{T_i^0} \right] \quad (1)$$

where superscript ℓ refers to the condensed phase, while $x_i^\ell, \gamma_i^\ell, \Delta_f H_i^0$ and T_i^0 respectively, are the molfraction, activity coefficient, enthalpy of fusion and melting temperature of eutectic phase, i ($=1,2$); T represents liquidus temperature of the phase mixture at molfraction composition, x_i^ℓ , and R is a gas constant. Ideal liquidus temperatures of the binary systems are calculated from Eq.(1) by putting $\gamma_i^\ell=1$ and are recorded in Tables 2-7 and plotted by dotted lines in Figs. 1-6.

The experimental and theoretical solidus-liquidus equilibrium curves in each system evidentially do not coincide with each other confirming its deviation from ideality and the occurrence of molecular interactions between condensed interphase molecules as well. With a view to achieve physical understanding and the quantitative idea of molecular interactions, the activity coefficients of the eutectic phases either side of solidus-liquidus equilibrium

curve of each system are computed as a function of their respective temperature and composition from Eq.(1) and thereby, inserted in Eqs. (2) and (3)[11,22]:

$$RT\ln\gamma_1^\ell = A(x_2^\ell)^2 + B(x_2^\ell)^2 + C(x_2^\ell)^3 \quad (2)$$

$$RT\ln\gamma_2^\ell = A'(x_1^\ell)^2 + B'(x_1^\ell)^2 + C'(x_1^\ell)^3 \quad (3)$$

The constants A, B, C, A', B' and C' evaluated with the application of least-squares method are provided in the Table 8. The application of Gibbs-Duhem transformation would determine $\ln\gamma_1^\ell$ and $\ln\gamma_2^\ell$ for each experimental composition comprising of molfractions x_1^ℓ and x_2^ℓ , with liquidus temperature T of the same branch of the curve. This implies that the corresponding equations for Eqs. (2) and (3) at the same temperature could readily be transformed to in the following forms:

$$RT\ln\gamma_1^\ell = (A' - 2B)x_1^\ell - A\ln x_1^\ell + (B' - \frac{3}{2}C)(x_1^\ell)^2 + C'(x_1^\ell)^3 + B' - A' + \frac{C'}{2} \quad (4)$$

$$RT\ln\gamma_2^\ell = (A - 2B)x_2^\ell - A\ln x_2^\ell + (B - \frac{3}{2}C)(x_2^\ell)^2 + C(x_2^\ell)^3 + B - A + \frac{C}{2} \quad (5)$$

The physical significance of the transformation is that Eqs. (4) and (5) can, respectively, predict quantitative values of $\ln\gamma_1^\ell$ and $\ln\gamma_2^\ell$ as functions of x_1^ℓ and x_2^ℓ for any composition at the same liquidus temperature, T . The computed activity coefficient data for the eutectic phases in various binary mixtures of all the systems at respective liquidus temperatures are recorded in Table 9 (a-f). The activity coefficient data can further facilitate the process of reckoning the excess functions, viz., G^E, S^E and H^E of pre-, post-, and eutectic compositions along with the excess chemical potentials of the eutectic members; $\mu_i^E, i(=1,2)$ at the same liquidus temperature T , in all the systems at constant pressure using the following relations[9,13]:

$$G^E = RT[x_1^\ell \ln\gamma_1^\ell + x_2^\ell \ln\gamma_2^\ell] \quad (6)$$

$$S^E = -R \left[x_1^\ell \ln\gamma_1^\ell + x_2^\ell \ln\gamma_2^\ell + T x_1^\ell \left(\frac{\partial \ln\gamma_1^\ell}{\partial T} \right)_P + T x_2^\ell \left(\frac{\partial \ln\gamma_2^\ell}{\partial T} \right)_P \right] \quad (7)$$

$$H^E = -RT^2 \left[x_1^\ell \left(\frac{\partial \ln\gamma_1^\ell}{\partial T} \right)_P + x_2^\ell \left(\frac{\partial \ln\gamma_2^\ell}{\partial T} \right)_P \right] \quad (8)$$

$$\mu_i^E = RT\ln\gamma_i^\ell \quad (9)$$

The values of $\left[\frac{\partial \ln\gamma_i^\ell}{\partial T} \right]_P (i=1,2)$ for any binary system can be determined from the slopes of the liquidus lines obtained by plotting the activity coefficients $\ln\gamma_1^\ell$ and $\ln\gamma_2^\ell$ of the eutectic phases in variable compositional mixtures against their liquidus temperature T , for that system. The slopes for each system determined in this manner were utilized in computing the excess functions, viz., G^E, S^E, H^E and $\mu_i^E, i(=1,2)$ by Eqs. (6), (7), (8) and (9) which are recorded in the Table 9(a-f). The reckoned excess functions for the binary naphthalene-*o*-nitrophenol, diphenylamine- α -naphthol, benzil-diphenyl and cadmium-bismuth, tin-cadmium and tin-lead eutectic systems are also represented in Figs.7-12 with a definite purpose to reveal qualitative variation aspects of the excess functions over the entire molfraction composition range in general and the eutectic composition in particular (Tables 2-7).

Table 8: Independent parameters of the systems

System	A	B	C	A'	B'	C'
naphthalene- <i>o</i> -nitrophenol	350.38	174.84	-49.025	1652.81	-17998	7313.87
diphenylamine- α -naphthol	-2921.52	15100.00	-304.43	16291.64	-24345	-16428.57
benzil-diphenyl	-4.0012	36.89	-62.50	-26268.43	-921.25	.071337
cadmium-bismuth	5590.30	-17600	3245.28	-921.25	56.43	345.40
tin-cadmium	4859.23	-15334.50	2820.90	-801.62	49.07	301.20
tin-lead	77.6	2848.66	-6007.9	453.05	-80.25	-5177.70

Table 9(a): Activity coefficient and excess thermodynamic functions for the binary system naphthalene (1)-*o*-nitrophenol (2)

Molfraction of component (1)	Liquidus temperature (K)	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^E (kJmol ⁻¹)	Excess entropy S^E (J mol ⁻¹ K ⁻¹)	H^E (J mol ⁻¹)	Chemical potential of component (1) μ_1^E (J mol ⁻¹)	Chemical potential of component (2) μ_2^E (J mol ⁻¹)
0.1	315.2	-0.0623	0.03532	0.12	-0.382	-0.406	-163.13	200
0.2	311.6	-0.0472	0.07509	0.079	-0.254	-0.146	-122.28	194.52
0.3	304.8	-0.0287	0.05626	0.077	-0.253	-0.114	-72.75	142.57
0.325 (e*)	303.7	-0.3006	0.02244	-0.314	1.035	0.329	-72.49	142.05
0.4	311.8	-0.3506	0.02618	0.263	0.844	0.159	92.26	58.17
0.5	321.3	0.04853	0.0371	-0.015	0.046	0.101	129.64	99.1
0.6	330.5	0.0643	0.0575	0.165	-0.5	-0.25	137.66	112.93
0.7	336.2	0.0274	0.0869	0.193	-0.575	-0.315	145.63	118.8
0.8	343.3	0.03458	0.1302	0.317	-0.925	-0.553	150.7	145.81
0.9	349	0.02566	0.2157	0.57	-1.636	-0.964	174	377.79

The values of G^E and S^E at eutectic point e*, by Guggenheim lattice theory are -1.40 kJmol⁻¹ and 4.50 Jmol⁻¹K⁻¹ respectively.

Table 9(b): Activity coefficient and excess thermodynamic functions for the binary system diphenylamine(1)- α naphthol(2)

Molfraction of component (1)	Liquidus temperature (K)	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^E (kJmol ⁻¹)	Excess entropy S^E (J mol ⁻¹ K ⁻¹)	H^E (J mol ⁻¹)	Chemical potential of component (1) μ_1^E (J mol ⁻¹)	Chemical potential of component (2) μ_2^E (J mol ⁻¹)
0.1	362.5	-4.84	-0.01	-1.47	0.00406	0.0018	-2.747	-14.589
0.2	355.7	-9.884	1.329	-2.7	0.0076	0.0033	-5.037	-29.229
0.3	349.7	-13.54	0.811	-10.15	0.0291	0.0262	-11.053	-39.372
0.4	341.7	-16.86	0.327	-18.59	0.545	0.0326	-35.421	-47.886
0.5	334.5	-20.04	-0.06	-27.95	0.084	0.148	-53.821	-55.731
0.6	325.4	-23.43	-0.5	-38.54	0.119	0.182	-75.32	-63.386
0.7	315.4	-27.15	-0.93	-50.57	0.161	0.209	-100.442	-71.193
0.7600 (e*)	311.7	-29.34	0.052	-57.73	0.186	0.246	-115.394	-76.033
0.8	314.7	-0.045	2.737	0.25	-0.0008	-0.0017	0.496	-0.117
0.9	321.8	-0.002	5.102	0.3	-0.00094	-0.0025	0.589	-0.0053

The values of G^E and S^E at eutectic point e*, by Guggenheim lattice theory are -15.16 kJmol⁻¹ and 4.87 Jmol⁻¹K⁻¹ respectively.

Table 9(c): Activity coefficient and excess thermodynamic functions for the binary system benzil (1)- diphenyl (2)

Molfraction of component (1)	Liquidus temperature (K)	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^E (kJmol ⁻¹)	Excess entropy S^E (J mol ⁻¹ K ⁻¹)	H^E (J mol ⁻¹)	Chemical potential of component (1) μ_1^E (J mol ⁻¹)	Chemical potential of component (2) μ_2^E (J mol ⁻¹)
0.1	336.5	1.046	0.0032	0.3	-0.892	-0.158	2926.35	8.95
0.2	333.1	-0.746	0.055	-0.28	0.841	0.137	-2065.96	152.31
0.3	325.9	-0.59	-0.00622	-0.49	1.505	0.479	-1598.62	-16.85
0.3950 (e*)	322	-0.69	-0.008	-0.57	1.773	0.906	-1847.2	-21.41
0.4	329.6	-0.3814	-0.00287	-0.42	1.275	0.24	-1044.87	-7.86
0.5	335.5	0.04823	0.00303	-0.06	0.179	0.05	134.53	8.45
0.6	344.8	-0.00329	-0.00199	-0.007	0.02	0.06	-9.43	-5.7
0.7	350.33	0.0281	-0.0353	0.026	-0.074	-0.274	81.83	-102.81
0.8	355.2	0.0509	0.0094	0.125	-0.353	-0.385	150.31	27.75
0.9	361	0.06261	0.00001	0.169	-0.47	-0.67	187.91	0.03

The values of G^E and S^E at eutectic point e*, by Guggenheim lattice theory are -1.85 kJmol⁻¹ and 5.73 Jmol⁻¹K⁻¹ respectively.

Table 9(d): Activity coefficient and excess thermodynamic functions for the binary system cadmium (1)–bismuth (2)

Mol fraction of component (1)	Liquidus temperature (K)	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^E (kJ mol^{-1})	Excess entropy S^E ($\text{J mol}^{-1}\text{K}^{-1}$)	H^E (J mol^{-1})	Chemical potential of component (1) μ_1^E (J mol^{-1})	Chemical potential of component (2) μ_2^E (J mol^{-1})
0.171	503.00	0.0685	-0.013	0.00083	-0.00166	-0.005	286.50	-58.12
0.309	478.00	0.0723	0.0206	0.145	-0.304	-0.312	287.32	81.86
0.440	443.00	0.0770	0.0163	0.158	-0.358	-0.594	283.59	60.03
0.505 (e*)	417.00	0.1530	-0.767	-1.24	2.978	1.826	530.44	-2660.52
0.656	466.00	0.0776	-1.057	-1.21	2.60	1.60	300.64	-4096.31
0.736	498.00	0.0597	-1.170	-1.09	2.19	0.62	247.18	-4844.64
0.815	530.00	0.0547	-1.211	-0.79	1.491	0.23	241.03	-5336.17
0.887	553.00	0.0294	-1.098	-0.45	0.814	0.14	135.17	-5050.04
0.952	573.00	0.0042	-0.563	-0.11	0.192	0.02	20.00	-2685.42

The values of G^E and S^E at eutectic point e*, by Guggenheim lattice theory are $-2.19 \text{ kJ mol}^{-1}$ and $5.25 \text{ J mol}^{-1}\text{K}^{-1}$ respectively.

Table 9(e): Activity coefficient and excess thermodynamic functions for the binary tin (1)- cadmium (2) system

Mol fraction of component (1)	Liquidus temperature (K)	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^E (kJ mol^{-1})	Excess entropy S^E ($\text{J mol}^{-1}\text{K}^{-1}$)	H^E (J mol^{-1})	Chemical potential of component (1) μ_1^E (J mol^{-1})	Chemical potential of component (2) μ_2^E (J mol^{-1})
0.1002	567.00	-0.0168	-1.27	1.72	-0.51	-0.31	-79.20	-5986.83
0.2003	535.00	-1.007	-0.035	1.41	-0.20	-0.08	-4479.13	-155.68
0.3003	509.00	-0.727	-0.054	1.10	0.31	0.05	-3076.54	-228.52
0.4000	483.00	-0.1600	-0.0991	0.72	0.63	0.20	642.51	-397.95
0.5001	468.00	-0.2719	-0.0933	-0.31	1.62	1.10	-1057.95	-363.03
0.5999	455.00	-0.0870	-0.1052	-1.20	2.23	1.60	-329.11	-397.96
0.7100(e*)	449.00	0.0412	-0.1162	-3.20	3.20	2.10	153.80	-433.77
0.8000	465.00	0.0895	-0.1179	-2.71	1.79	1.31	380.80	-455.80
0.9003	490.00	0.0823	-0.1133	-1.80	1.41	1.10	335.28	-461.57

The values of G^E and S^E at eutectic point e*, by Guggenheim lattice theory are $-3.95 \text{ kJ mol}^{-1}$ and $5.60 \text{ J mol}^{-1}\text{K}^{-1}$ respectively.

Table 9(f): Activity coefficient and excess thermodynamic functions for the binary tin(1) – lead(2) system

Mol fraction of component (1)	Liquidus temperature (K)	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's Free Energy G^E (kJ mol^{-1})	Excess entropy S^E ($\text{J mol}^{-1}\text{K}^{-1}$)	H^E (J mol^{-1})	Chemical potential of component (1) μ_1^E (J mol^{-1})	Chemical potential of component (2) μ_2^E (J mol^{-1})
0.1	547.00	-0.42	0.009	-0.15732	0.287	-0.341	-1910.06	40.93
0.2	493.00	-0.48	0.012	-0.36069	0.732	0.186	-1967.42	49.18
0.3	443.00	-0.499	0.014	-0.51526	1.164	0.392	-1837.86	51.56
0.4	399.00	-0.471	0.026	-0.57322	1.438	0.541	-1562.44	86.25
0.5 (e*)	367.00	-0.301	-0.251	-0.82919	2.261	0.597	-915.37	-762.80
0.6	397.00	-0.031	-0.270	-0.29507	0.7444	0.456	102.32	-891.17
0.7	428.00	-0.029	-0.250	-0.19418	0.4553	0.2331	102.95	-887.51
0.8	457.00	0.027	-0.210	-0.7826	0.1715	0.115	102.58	-797.89
0.9	486.00	0.022	-0.012	0.31516	-0.065	-0.074	88.89	-484.87

The values of G^E and S^E at eutectic point e*, by Guggenheim lattice theory are $-1.93 \text{ kJ mol}^{-1}$ and $5.268 \text{ J mol}^{-1}\text{K}^{-1}$ respectively.

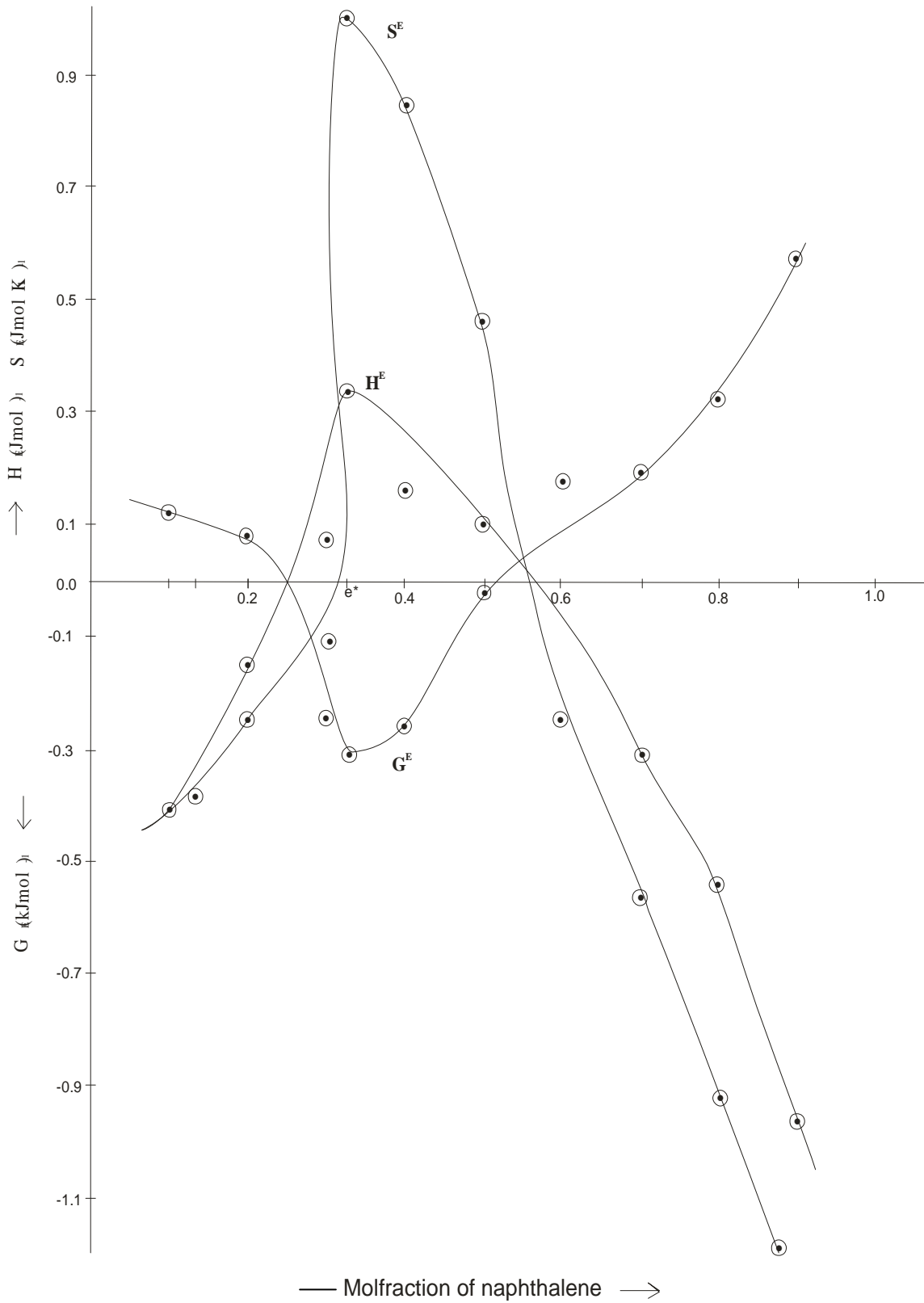


Fig. 7. Excess thermodynamics functions G^E , S^E and H^E for naphthalene-*o*-nitrophenol system
 e^* : eutectic composition

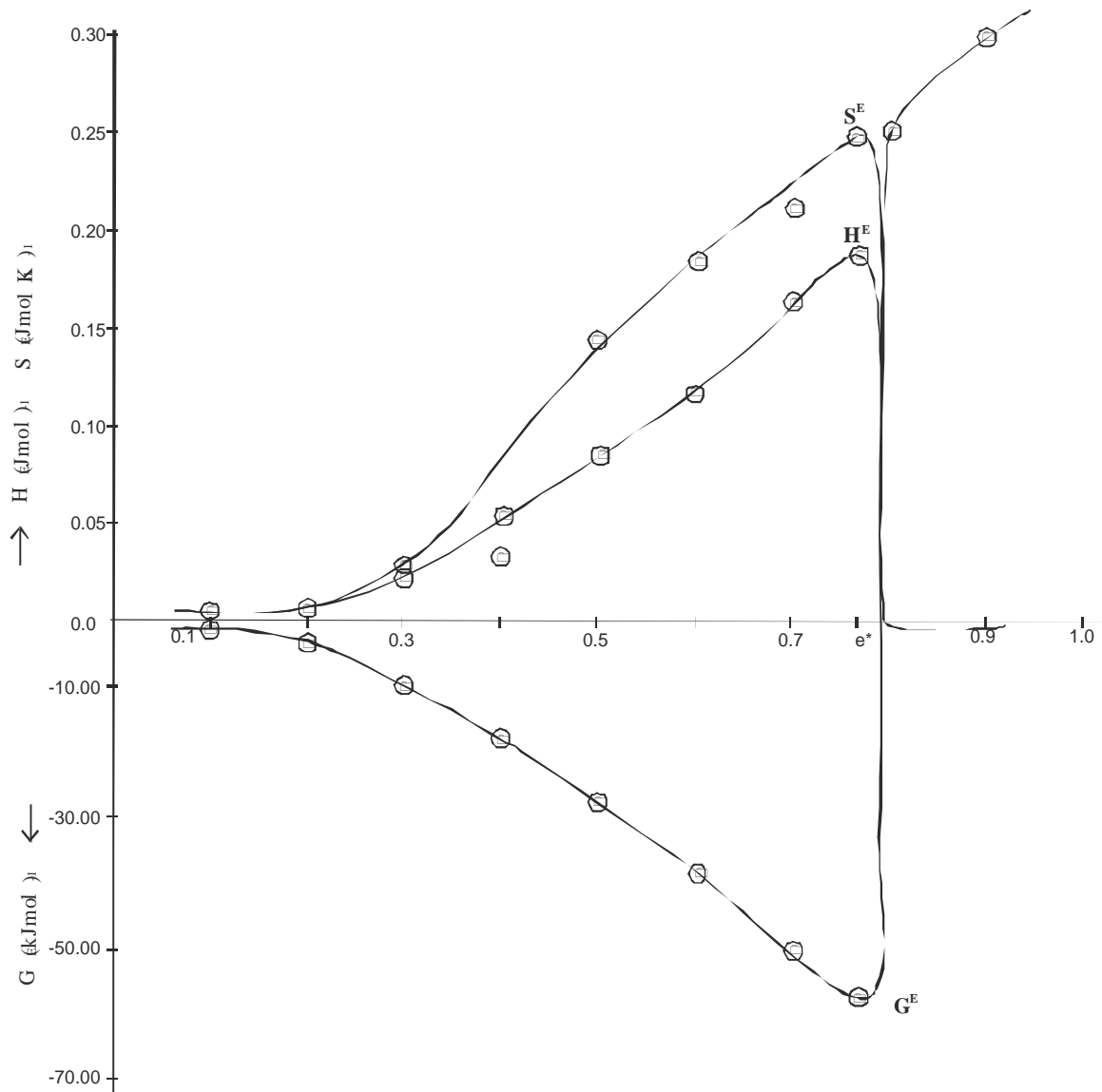


Fig. 8. Excess thermodynamics functions G^E , S^E and H^E for diphenylamine- α -naphthol system
 e^* : eutectic composition

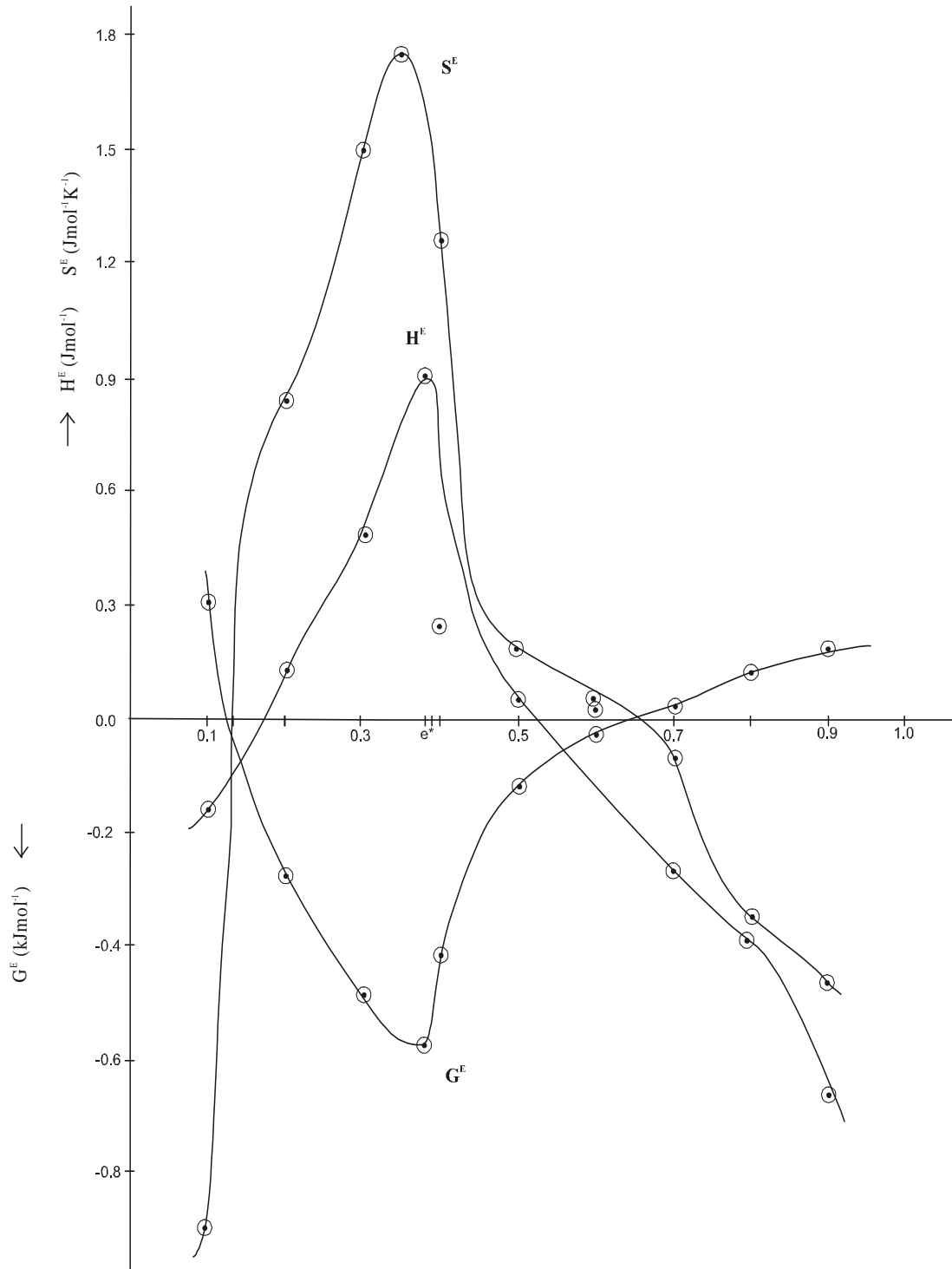


Fig. 9 . Excess thermodynamics functions G^E , S^E and H^E for benzil–diphenyl system.

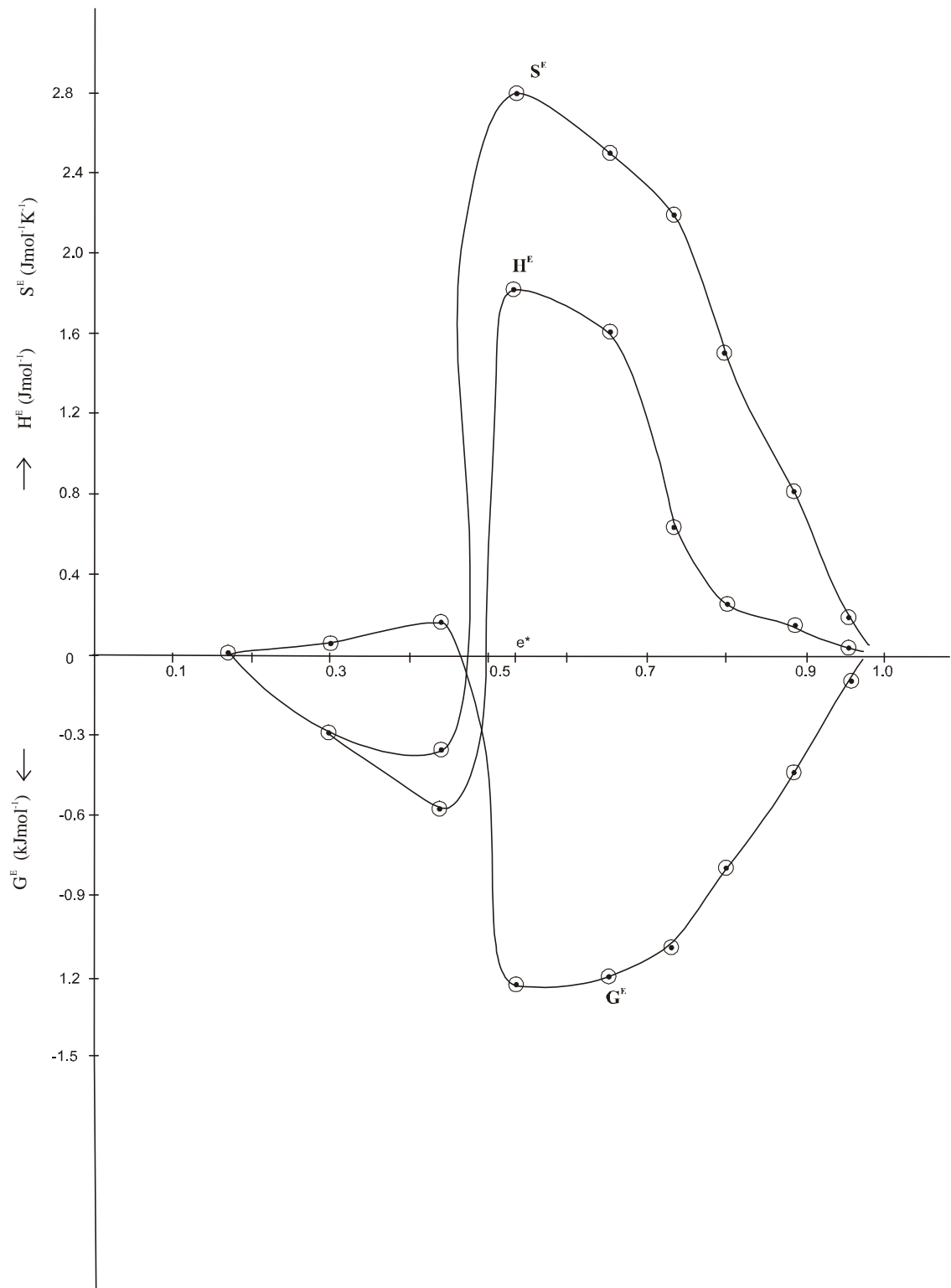


Fig. 10. Excess thermodynamic functions G^E , S^E and H^E for Cd-Bi eutectic system

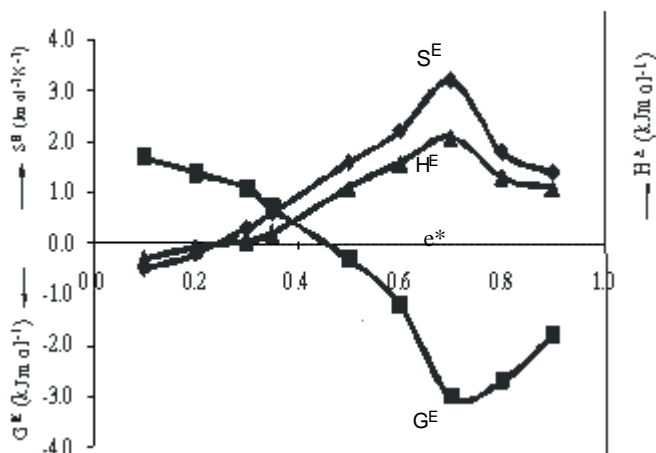


Fig. 11. Excess thermodynamic functions G^E , S^E and H^E for Sn–Cd eutectic system
 e^* : eutectic composition

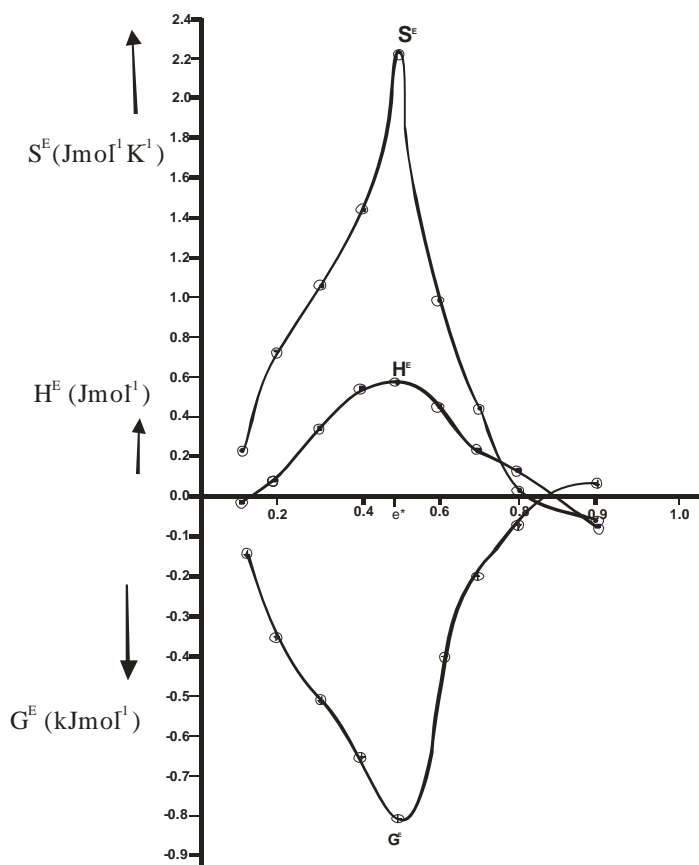


Fig. 12. Excess thermodynamic functions G^E , S^E and H^E for Sn–Pb eutectic system
 e^* : eutectic composition

DISCUSSION

The eutectic compositions (e^*) and eutectic temperatures (T_e) of binary naphthalene-*o*-nitrophenol, diphenylamine- α -naphthol and benzil-diphenyl, cadmium- bismuth, tin – cadmium and tin-lead systems manipulated from their respective diagrams of state and later experimentally verified are given numerically in

Tables 2-7 and theoretically represented in Figs.1-6. The perusal of both quantitative (Tables 9 a-f) and qualitative (Figs. 7-12) analyses explores that the excess free energy of mixing, G^E would decrease gradually either side of solidus-liquidus equilibrium curves (Figs. 1-6) and furnish minima at the eutectic compositions. Evidentially, the variation of G^E over the entire molfraction composition range of each experimental system is consistent with the miscibility criteria of spontaneity[23], because the mixing of the eutectic phases of any binary system would progress only if every infinitesimal change in the composition of that system is accompanied by a decrease in free energy. Obviously, the miscibility criteria explained the cause of most negative value of Gibbs free energy, G^E at the eutectic composition. On the contrary, the excess entropy, S^E would acquire maxima at the eutectic composition of the experimental systems which should be there because of its obedience to the miscibility criteria. The explanation of the maximum value of S^E , at the eutectic composition, lies in the concept that the most probable configuration of the eutectic interphase molecules in the condensed state, occurs at this very composition (e^*) and temperature (T_e) owing to the co- existence of three phases (two solidus and one liquidus) in equilibrium. Further, the minimum and maximum values of G^E and S^E respectively at the eutectic compositions implicitly, predict that the experimental binary systems follow the criteria of spontaneity and Planck hypothesis, $S = k \ln w$ where k and w , respectively, being the Boltzmann constant and the weight of configuration which is estimated the most probable one at the eutectic composition since the phase molecules in the eutectic compositions obey Weibull distribution. It may be pertinent to mention here that the number of distinct arrangements of phase molecules in any compositional configuration do determine the weight of that configuration, and the most probable compositional configuration is characterized by optimum value of w . The excess chemical potentials, u_i^E ($i=1,2$), of the eutectic phases numerically signify the permissible equilibrium levels in the condensed states of the experimental binary systems. Likewise, the excess enthalpy of mixing, H^E , offers supporting evidence to strengthen the observations of G^E and S^E for the experimental binary systems to be far from being ideal, since H^E is found nontrivial for the systems. Further, the Table 9(a-f) records positive and negative magnitudes of H^E which are respectively, consistent with the positive and negative deviations from the ideal regions of the systems. Besides, the higher value of H^E for the eutectic composition in each system conforms to the most stable composition in the molfraction compositional range at all liquidus temperatures covered by solidus-liquidus phase equilibrium curve. The computational procedure of the excess functions from enthalpies of fusion data of the eutectic phases confirms their reliability and authenticity in predicting the nonideal nature of liquidus solutions of the binary systems, since the excess functions express their obedience to the miscibility criteria and Planck formulation, thus provides quantitative idea of the molecular interactions.

Moreover, the Guggenheim lattice theory[24], would evidentially offer supporting evidence to the occurrence of molecular interactions in terms of excess thermodynamic functions. The theory speaks that the activity coefficients of the eutectic mixtures can be computed from the following Eqs. [9,13, 21,28]:

$$RT \ln \gamma_i^\ell = A(1 - x_i^\ell) + B(1 - x_i^\ell)^2 \quad (10)$$

The activity coefficient data accomplished by Eq. (10) inferred that the experimental systems are not regular. Imagine an equilibrium composition of a binary system which shows complete miscibility in solidus-liquidus regular solution at liquidus temperature, T at which applicability of the Guggenheim lattice theory is represented by Eq. (11):

$$-\ln \frac{x_i^\ell \gamma_i^\ell}{x_i^S \gamma_i^S} = \frac{\Delta_f H_i^0}{R} \left[\frac{1}{T} - \frac{1}{T_i^0} \right] \quad (11)$$

where x_i^ℓ , γ_i^ℓ , $\Delta_f H_i^0$ and T_i^0 are already defined for the eutectic phase i ($=1,2$) with the molfraction x_i^S and activity coefficient γ_i^S in the solidus phase in equilibrium with the liquidus phase at temperature T . The excess functions G^E and S^E calculated by Eqs. (6) and (7) for the eutectic compositions of the binary systems are not found in agreement with their values obtained by Eqs. (12) and (13), which are the extraction of Eq. (11) presuming the nature of eutectic mixture to be regular:

$$G^E = (x_1^\ell)_m \Delta_f H_1^0 \left(\frac{T_m - T_1^0}{T_1^0} \right) + (x_2^\ell)_m \Delta_f H_2^0 \left(\frac{T_m - T_2^0}{T_2^0} \right) \quad (12)$$

$$S^E = - \left[(x_1^\ell)_m \Delta_f H_1^0 \left(\frac{T_m - T_1^0}{T_m T_1^0} \right) + (x_2^\ell)_m \Delta_f H_2^0 \left(\frac{T_m - T_2^0}{T_m T_2^0} \right) \right] \quad (13)$$

$$H^E = G^E - T_m S^E = 0 \quad (14)$$

the subscript ' m ' represents the minima in solidus-liquidus equilibrium curves. Eqs. (12) and (13) expressing their obedience to the Guggenheim lattice theory respectively, yield minimal value of G^E and maximal value of S^E for regular eutectic mixtures presumed for in each experimental system compared to the value attained by the nonideal

counterparts as revealed by Eqs. (6) and (7). For instance, G^E and S^E values for the nonideal eutectic mixture of naphthalene-*o*-nitrophenol system obtained by Eqs. (6) and (7), respectively, are $-0.314 \text{ kJ mol}^{-1}$ and $1.035 \text{ Jmol}^{-1}\text{K}^{-1}$. On the contrary, the regular counterpart is explored to have respective values of the magnitude of -1.40 kJmol^{-1} and $4.50 \text{ Jmol}^{-1}\text{K}^{-1}$ computed by Eqs. (12) and (13). An Insight analysis indicates that the value of G^E obtained by Eq.(12) for regular eutectic melt is more negative than its value computed by Eq.(6), a physical phenomenon which is consistent with the criteria of spontaneity (miscibility) that the formation of regular eutectic mixture progresses only if every infinitesimal change in composition shows a decrease in Gibbs free energy implying certainly low compared to that of a nonideal eutectic mixture. Contrarywise, Eq.(13) yields S^E which is more positive for the regular eutectic compositional melt because of the most probable configuration of the phase molecules that occurs in the regular eutectic melt predominating the weight of phase molecules' configuration in the nonideal eutectic melt. This implies that molecular interactions exhibit the ability to uphold the inequality $w_{\text{reg}} > w_{\text{real}}$, where w_{reg} and w_{real} , respectively, represent the number of distinct arrangements of interphase molecules in the regular and nonideal eutectic melts. The conformity of all the experimental binary eutectic systems with the criteria of miscibility and Planck formulation explicitly, evinces the reliability of thermodynamic analysis and thereby, the computation process of excess functions using lone enthalpy of fusion data of constituent phases. Besides, the negative and positive numerical signs of the excess functions, viz., G^E is negative, and S^E and H^E are positive, for the eutectic compositions of binary naphthalene-*o*-nitrophenol, diphenylamine- α -naphthol, benzil-diphenyl, the metallic cadmium-bismuth, tin-cadmium and tin-lead binary systems, predict that these compositions being endothermic in nature from thermochemistry point of view, represent the most stable regions in the domain of temperature-compositions range of phase equilibria spatial fidelity.

CONCLUSION

Excess thermodynamic functions are discovered the best tool to explain the deviations of binary condensed phase eutectic systems from their ideal behaviour since these functions provide quantitative idea about the nature of molecular interactions occurring in binary condensed variable compositional phase. It may be pertinent to mention here that direct experimental techniques for measuring excess thermodynamic functions are firstly not developed and secondly, their design seem by no means simple. Alternatively, a model is developed wherein thermodynamic analysis of solidus-liquidus equilibrium extracts the excess thermofunctions which are reliable because all the parameters facilitated the reckoning procedure were experimentally determined quantities. An interpretation for the reliability of excess thermofunctions is comprehensively presented and essentially authenticated by their obedience to the Criteria of spontaneity and Planck formulation over the entire temperature-composition range covered by the phase equilibrium curve. The applicability of the Guggenheim lattice theory to the condensed eutectic compositional phase at the liquidus temperature is explicitly explained in the discussion that too offers supporting evidence to the reliability and existence of excess thermofunctions. The thermonature of the binary eutectic systems investigated in the present investigation is ascertain from the computed excess thermofunctions. A physical appearance drawn from the aesthetic ability of the excess thermofunctions at variable temperature and composition covering the whole range as the spatial coordinates associated with the diagram of state for a binary eutectic system leads to an ardently conclusion that translates the development of an auxillary device to study the solidus-liquidus phase equilibria especially of binary condensed eutectic systems.

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