Excess Properties of Lennard-Jones binary mixtures from computer simulation and theory

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Monte Carlo simulation and theory are used to calculate the excess thermodynamic properties of binary mixtures of spherical Lennard-Jones molecules. We study the excess functions of three binary mixtures characterised by the following size and dispersive energy ratios: (1) $(\sigma_{22}/\sigma_{11})^3 = 2$ and $\epsilon_{22}/\epsilon_{11} = 2$; (2) $(\sigma_{22}/\sigma_{11})^3 = 1$ and $\epsilon_{22}/\epsilon_{11} = 2$; and (3) $(\sigma_{22}/\sigma_{11})^3 = 1/2$ and $\epsilon_{22}/\epsilon_{11} = 2$. In all cases, the unlike size parameter, σ_{12}, is kept constant and equal to the value given by the Lorentz combining rule ($\sigma_{12} = (\sigma_{11}+\sigma_{22})/2$). However, different unlike dispersive energy parameter values are considered through the following combining rules: (a) $\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}}$ (Berthelot rule); (b) $\epsilon_{12} = \epsilon_{11}$ (association); and (c) $\epsilon_{12} = \epsilon_{22}$ (solvation). The pressure and temperature dependence of the excess volume and excess enthalpy is studied using the NpT Monte Carlo simulation technique for all the systems considered. Additionally, the simplest conformal solution theory is used to check the adequacy of this approach in predicting the excess properties in a wide range of thermodynamic conditions and variety of binary mixtures. In particular, we have applied the van der Waals one-fluid theory to describe Lennard-Jones binary mixtures through the use of the Johnson *et al.* (*Mol. Phys.* **78**, 591 (1993)) Helmholtz free energy. Agreement between simulation results and theoretical predictions is excellent in all cases and thermodynamic conditions considered. This work confirms the applicability of the van der Waals one-fluid theory in predicting excess thermodynamic properties of mixtures of spherical molecules. Furthermore, since binary mixtures of spherical Lennard-Jones molecules constitute the reference fluid to be used in perturbation theories for complex fluids, such as the Statistical Association Fluid Theory (SAFT), this work shows clearly the applicability of the conformal solution theory within the framework of SAFT for predicting excess functions.

1 Introduction

Excess thermodynamic properties provide an important and fundamental information on the intermolecular interactions between the species forming binary and multicomponent systems. From an experimental point of view, scientists tabulate the results of their measurements on the thermodynamic properties of non-ideal mixtures is this way. Such data is used extensively in a wide variety of scientific and technical fields: chemistry, spectroscopy and chemical engineering.[1–3] From a theoretical point of view, the excess thermodynamic functions constitute also a valuable information since classical equations of state and other advanced modelling techniques, such as those based on statistical mechanics, lead naturally to the prediction of theoretical values of excess properties.[4] Since the excess functions are more sensitive than phase equilibria to the molecular details, its prediction provides an excellent way to check if theoretical approaches are suitable for predicting the thermodynamic behaviour of a given system.

Abundant experimental data of the constant pressure excess properties of binary mixtures, such as excess enthalpies, H^E, excess volumes, V^E, and excess Gibbs free energies, G^E, have been accumulated in the literature.[4] It is generally believed that mixtures in which intermolecular forces are not characterised by strong and specific interactions exhibit excess functions that are fairly close to those of the ideal mixture and its behaviour can be described accurately by the regular solution theory concepts proposed by Guggenheim[5] and Hildebrand-Scatchard[6] . However, the theoretical predictions obtained from this approach have been only verified for simple liquid mixtures at relatively low room temperature and low pressures (practically near zero pressure). During last years there have been a great development in specific topics, such as critical phenomena, supercritical fluids and physical properties at ultra high pressures, in which thermodynamic conditions cover wide ranges of temperature and pressure.[7] Experimental data in general, and excess properties in particular, often are not available at these extreme conditions of temperatures and pressures. In addition, such data may be difficult and expensive to obtain experimentally in some cases. In this situation, an equation of state or any other theoretical approach is highly desirable.

Correlations and macroscopic equations traditionally used in the chemical industry are not able to predict correctly the thermodynamic behaviour of fluid mixtures at conditions far away from which the experimental data is correlated, even for simple systems. Numerical correlations, such as the Redlich-Kister equation,[8] have parameters with no physical meaning; more sophisticated theories, as UNIQUAC,[9,10] NRTL,[10,11] or DISQUAC,[10,12] are based on the quasi-chemical approach introduced by Guggenheim,[13] which postulates that the nonidealities in fluids could be assigned to the existence of nonrandom mixing at the molecular level. The equations based on such theories, although can account for accurately the excess properties of a great number of fluid mixtures at thermodynamic conditions well below their critical points, are not of practical use over the whole fluid range. In addition, excess properties based on volumetric magnitudes, such as the excess volume, can not be described by these models since they are based on the assumption of a grid lattice model.

Molecular-based theories constitute alternative methods that describe correctly the thermodynamic behaviour and phase equilibria of systems as complex as chainlike mixtures, associating fluids, polymer solutions and reacting systems. They are based on the knowledge of the intermolecular interaction forces between the molecules that form the system. See the book of Sengers *et al.*[14] for recent developments in equations of state. These forces depend on molecular parameters with physical meaning, as molecular sizes and dispersive energies. Since they are microscopic, they do not depend on thermodynamic conditions, as pressure, temperature and composition. This leads to theories with high predictive power far away from conditions at which the molecular parameters are correlated. Molecular methods can be classified in two different types: molecular simulations and analytical theories.[15,16] Molecular simulations can be used to check if a given intermolecular potential is suitable for describing different systems, as well as to test the accuracy of a theory.[17,18] In this later use, molecular simulations constitute a valuable tool because they allow to test the approximations made to obtain analytical molecular-based equations of state.[17,18]

Major excess thermodynamic properties of spherical molecules interacting through the Lennard-Jones potential have been calculated using Monte Carlo simulation. However, some of the results obtained from molecular simulation may not be reliable because the thermodynamic properties of each component, as well as those corresponding to the mixtures, are determined separately. Therefore, it may occur a cancellation or magnification of errors. Special care should be taken for the calculation of the excess free energy. As it is well known, the free energy is probably the most difficult magnitude to calculate from molecular simulation.[19,20] One of the most reliable routes to evaluate the free energy is based on the coupling parameter charging approach introduced by Kirkwood.[21] McDonald[22,23] and Singer and Singer[24] were the first to use the coupling parameter method in context of Monte Carlo simulation, although the original version required the values of the free energies of the pure components. These authors have performed a detailed study to understand the effect of molecular parameters, such as the segment size and dispersive energy, of binary mixtures of Lennard-Jones spheres on the principal excess functions. They have shown that the Lorentz-Berthelot combining rules can predict negative values of all three major excess functions (V^E, H^E, G^E) for particular values of the molecular parameters. In general, G^E is more positive when the dispersive energy ratio $\epsilon_{12}/\epsilon_{11}$ is decreased; for molecules with equal dispersive energies, $\epsilon_{11} = \epsilon_{22}$, G^E becomes more negative with decreasing values of the σ_{12}/σ_{11} ratio.[4,22–24] A similar behavior is found by these authors for the excess molar enthalpy and excess molar volume.[4,22–24]

The method implemented by McDonald and Singer and Singer has been improved and used in late 1980s and the 90s by several authors.[25] Nowadays, this method constitutes a highly accurate molecular simulation procedure for obtaining the excess free energies of a great variety of systems. More recently, Fotouh and Shukla[26,27] have performed NpT molecular dynamic simulations to obtain all three major excess thermodynamic properties of binary and ternary mixtures of Lennard-Jones spheres. They have also considered two-center Lennard-Jones molecules and point quadrupolar interactions, and studied the effect of the molecular elongation and quadrupole on excess properties.

Nakanishi and co-workers have extensively studied the structure and thermodynamic properties, including the excess behaviour, of supercritical fluids using Monte Carlo simulation techniques.[28] In particular, they have calculated the excess Helmholtz free energy, local structure and other thermodynamic functions at nearly zero pressire,[29] as well as the equation-of-state behaviour of binary mixtures of spherical Lennard-Jones molecules.[30] Especially relevant for the present study are the works of Fujihara and Nakanishi in which the excess enthalpies of binary mixtures of Lennard-Jones spheres are obtained at very high pressure[31] and near or in the supercritical region.[32]

In addition to the molecular simulation techniques, the analytical theories constitute an alternative method to obtain reliable results from a molecular perspective.[15] For an excellent review of the most sophisticated theories based on a microscopic point of view see the book of Sengers *et al.*[14] One of the most simple theoretical approaches and easy to apply for describing the thermodynamic properties of mixtures in which only pairwise interactions following the same functional form are accounted for is the conformal solution theory. The simplest approach within this framework is the well known one-fluid approximation.[15] This is a zeroth-order theory in which the properties of the mixture, apart from the ideal terms, are taken to be those of a single, hypothetical, pure fluid. There exist different approximations in the literature. The crudest approach is the random mixing approximation due to Prigogine,[34] which can be derived from the assumption that all radial distribution functions in the mixture are identical. Leland *et al.*,[35] based on the works of Henderson and Leonard[36] and MacGowan *et al.*,[37] have assumed that the pair radial distribution function in the mixture scales with the molecular size for all the species, and also forced the agreement between the long-wavelength number density fluctuations in the hypothetical fluid and the mixture. These two assumptions lead to the well known van der Waals one-fluid theory. It is possible in principle to improve the one-fluid approximation introducing an ideal mixture of two hipothetical substances, instead of a single fluid, to describe the mixture properties. However, this approach produces inconsistencies on the critical region of fluid mixtures.[4,38]

The van der Waals one-fluid formalism has been applied by different authors to describe the thermodynamic properties and phase equilibria of binary and ternary mixtures of Lennard-Jones molecules. See for instance the works of Panagiotopoulos and co-workers.[39–41] It was generally believed that the van der Waals one-fluid theory can be only applied to described the thermodynamic properties of mixtures with components that have similar size and energy parameters, but several works indicate that the theory is able to predict accurately the thermodynamic properties and phase equilibria for highly asymmetric systems and mixtures deviating from the Berthelot rule.[39–41]

The aim of the present work is twofold. First, we obtain the major excess thermodynamic properties of asymmetric binary mixtures of Lennard-Jones spherical molecules with different combining rules in a wide range of temperatures and pressures, including the supercritical region and thermodynamic states at ultra high pressure, using Monte Carlo simulation. Second, we use the simplest conformal solution theory for binary mixtures of spherical molecules, namely, the van der Waals one-fluid theory, to check the accuracy of this theoretical approach in predicting excess thermodynamic properties of Lennard-Jones mixtures. The results obtained here constitute a valuable information since provide new simulation data at thermodynamic conditions at which experiments are difficult or impossible to be performed, and hence, it gives important information about the behaviour of the excess properties at such extreme conditions. Also, it shows clearly the applicability range of the van der Waals one-fluid theory to predict excess functions of binary mixtures of spherical fluids. This last point is especially relevant for predicting excess properties and other thermodynamic functions corresponding to more complex systems that can be described using molecular equations of state based on perturbations theories over spherical fluids, such as the Statistical Associating Fluid Theory (SAFT) approach.[42–50] Since the successful prediction of thermodynamic properties from this theory requires a precise description of the reference spherical fluid, it is important to know the range of thermodynamic conditions and systems for which the reference fluid can be described with confidence.

The rest of the paper is organised as follows: in section 2 we present the most relevant features of the Lennard-Jones model and the van der Waals one-fluid theory, molecular simulation details are described in section 3, followed by results and discussion in next section. Finally, conclusions are presented in section 5.

2 Molecular model and theory

The systems studied in the present work are based on the Lennard-Jones intermolecular potential, in which pairwise interactions between two spherical molecules separated a distance r is given by

$$\phi(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \tag{1}$$

where σ_{ij} and ϵ_{ij} are the size and the dispersive energy between spherical molecules i and j, respectively.

In this work we consider fluid mixtures which can be named in a general form as X-y-z or simply y-z, where X depends on the the combining rules for the unlike interactions, y represents the dispersive energy ratio, $\epsilon_{22}/\epsilon_{11}$, and z corresponds to the size ratio parameter, $(\sigma_{22}/\sigma_{11})^3$. In particular, we have considered three different systems, X-2-2, X-2-1, and X-2-(1/2). The unlike intermolecular interactions are determined by the values of the σ_{12} and ϵ_{12} parameters. We use the Lorentz combining rule for the unlike size of the mixture in all cases,

$$\sigma_{12} = \frac{(\sigma_{11} + \sigma_{22})}{2} \tag{2}$$

We also consider three different types of mixtures defined by the following unlike dispersive energies: X=LB (Berthelot), in which the unlike energy is given by $\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}}$), X=A (association), with the unlike dispersive energy $\epsilon_{12} = \epsilon_{11}$ and X=S (solvation), where the unlike energy parameter is given by $\epsilon_{12} = \epsilon_{22}$. Care must be taken with the nomenclature used in this work to name mixtures in which $\epsilon_{12} = \epsilon_{11}$ and $\epsilon_{12} = \epsilon_{22}$. In both cases, interactions between both components are spherically symmetric, and no specific interactions, such as hydrogen bonding or other type of association, exist. The interaction between unlike components for A-y-z systems is unfavourable: the component 2, which has stronger interaction in its pure state, tends to "self-associate" in the mixture (i.e., component 2 "likes" to be close to molecules of the same species and "unlikes" to be close to molecules 1). Due to that, these mixtures can be considered as a simplified *association* mixture model. Contrary, the unlike interactions for S-y-z systems are as strong as those between molecules of component 2, in such a way that 1-2 interactions are far more favourable that 1-1 interactions. In this situation, the coordination number of component 2 around component 1 becomes larger than average. Under this perspective, S-y-z systems can be regardered as a *solvation* mixture model. From the ensuing explanation is clear that the names *association* and *solvation* are only used as a nomenclature, and no real association or solvation occurs in these systems, in which only spherically symmetric interactions exist.

As in previous works, the parameter values correspond to those of argonlike molecules,[30–33] although this does not modify the general character of the approach. The size and energy parameters used in this work are presented in table 1.

The Helmholtz free energy of a binary mixture of spheres which interact through the Lennard-Jones intermolecular potential can be written as

$$A = A^{ideal} + A^{LJ} \tag{3}$$

where A^{ideal} is the ideal Helmholtz free energy of an ideal mixture of spherical molecules given by[15]

$$A^{ideal} = Nk_B T \left\{ \sum_{i=1}^{n} \Big[x_i \ln(x_i \rho \Lambda_i^3) \Big] - 1 \right\} \tag{4}$$

where $\rho = N/V$ is the density of the mixture, x_i is the molar fraction of component i, Λ_i its thermal de Broglie wavelength, and V the volume.

The residual Helmholtz free energy of a binary mixture of spherical molecules interacting through the Lennard-Jones intermolecular potential can be easily described using the conformal solution theory. The simplest approximation within this theoretical framework, which is applicable for fluid mixtures in which the pairwise intermolecular interactions follow the same functional form, is the van der Waals one-fluid theory.[15] In this theoretical approach a real mixture is considered as a single hypothetical fluid so that the residual Helmholtz free energy of the mixture is approximated by the residual Helmholtz free energy of a pure hypothetical fluid, with parameters σ_m and ϵ_m, calculated from[4,15,35]

$$\sigma_m^3 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sigma_{ij}^3 \tag{5}$$

$$\epsilon_m = \frac{\displaystyle\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \epsilon_{ij} \sigma_{ij}^3}{\displaystyle\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sigma_{ij}^3} \tag{6}$$

The residual Helmholtz free energy of the pure hypothetical fluid used in this work is that proposed by Johnson *et al.*[51] This free energy is based on an extended Benedict-Webb-Rubin equation of state that was fitted to simulation data for pure Lennard-Jones fluids over a broad range of temperatures and densities. Details of the simulations are reported elsewhere.[51]

Excess thermodynamic properties are calculated in the usual way from the mixture properties, i. e., as the differences between the actual thermodynamic functions of mixing and the corresponding values for the ideal mixture. Since the volume and enthalpy of mixing for the ideal mixture is equal to zero, the excess volume, V^E, and the excess enthalpy, H^E, are given simply by[4]

$$V^E = \Delta V_m = V_m - \sum_{i=1}^{n} x_i V_i \tag{7}$$

$$H^E = \Delta H_m = H_m - \sum_{i=1}^{n} x_i H_i \tag{8}$$

where ΔV_m and ΔH_m are the volume and enthalpy of mixing, V_m and H_m are the volume and enthalpy of the mixture, and V_i and H_i are the volume and enthalpy of the pure component i, respectively.

3 Monte Carlo simulation details

We have used the NpT (isothermal-isobaric) Monte Carlo simulation technique[19,20] following the scheme developed by McDonald[22,23] and Singer and Singer[24] to obtain the thermodynamic properties of binary mixtures of spherical Lennard-Jones molecules, such as the excess volume, V^E and the excess enthalpy, H^E, at constant pressure. All the simulations have been performed with a fixed number of molecules, $N = 500$.

The temperature, pressure and number of molecules are specified *a priori*, allowing the volume to fluctuate, as well as the internal configurational and chemical potential. Attempts to displace a molecule and attempts to change the volume of the simulation box are made to reach the internal and mechanical equilibrium, respectively. We have used periodic boundary conditions and the minimum image convention. The calculation of the configurational internal energy is performed in the usual way, truncating the Lennard-Jones interactions at half the box size, and adding the standard long range corrections, which have been applied during the course of the simulations. The simulations were divided in an equilibrium period of 10000 Monte Carlo steps, followed by 40000 Monte Carlo steps for averaging. The numerical values of the pure component properties are obtained as an average of five Monte Carlo runs which have different series of random numbers to each other. Uncertainties inherent to V^E and H^E can be estimated approximately by those associated with the molar enthalpies and volumes of the mixtures. In a previous work,[33] additional Monte Carlo simulations were carried out in order to estimate the uncertainties inherent in H^E and V^E. From these results is expected that the errors associated to the excess functions to be less than 20J/mol and less than 0.5cm^3/mol in H^E and V^E, respectively.

4 Results

We have obtained the excess properties of binary mixtures of spherical Lennard-Jones molecules using NpT Monte Carlo simulation and the van der Waals one-fluid theory. In particular, we consider the following size and dispersive energy ratios: (1) $(\sigma_{22}/\sigma_{11})^3 = 2$ and $\epsilon_{22}/\epsilon_{11} = 2$; (2) $(\sigma_{22}/\sigma_{11})^3 = 1$ and $\epsilon_{22}/\epsilon_{11} = 2$; and (3) $(\sigma_{22}/\sigma_{11})^3 = 1/2$ and $\epsilon_{22}/\epsilon_{11} = 2$. The critical temperatures and pressures of the pure substances studied in this work are shown in table 2. In all cases, the unlike size parameter, σ_{12}, is kept constant and equal to the value given by the Lorentz combining rule ($\sigma_{12} = (\sigma_{11}+\sigma_{22})/2$). However, different unlike dispersive energy parameter values are considered through the following combining rules: (a) $\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}}$ (Berthelot rule); (b) $\epsilon_{12} = \epsilon_{11}$ (association); and (c) $\epsilon_{12} = \epsilon_{22}$ (solvation). All mixtures are studied at three different temperatures, $T = 230, 250$ and 300K and several pressures, from $p = 30$ to 500atm, although in most cases the study has been extended up to $p = 1000$atm. All temperatures considered are above the critical temperatures of pure components; depending on the system, pressures correspond to subcritical and supercritical conditions, although for pressures higher than

100atm, all systems are in supercritical conditions (see table 2 for further datils). The excess functions are calculated from the thermodynamic properties of the mixtures as explained in section 2 from molecular simulation and theory. Comparison between both results are presented for all the systems considered and at all thermodynamic conditions under study. The results are presented in four different sections. In the first three sections we study separately the excess properties of the three binary systems considered, and in the last section, we study the temperature dependence of the excess properties.

4.1 2-1 systems

We consider first the 2-1 systems in which the segment size of both components are equal and the dispersive energy ratio given by $\epsilon_{22}/\epsilon_1 = 2$. These parameter values correspond to a system with a moderate asymmetry, and similar sets of parameters can be used to describe real systems. Figure 1 shows the excess volume and enthalpy corresponding to the system in which the unlike interactions are described via the Lorentz-Berthelot combining rules. As can be seen in figure 1a, the excess volume is profoundly affected by the pressure values. At low pressures, the excess volume is positive, nearly quadratic (although the maximum is shifted toward the more volatile component) and exhibits low values. As the pressure increases from 60atm to 100atm, the excess function increases an order of magnitude. If the pressure is further increased the excess volume decreases, although exhibits sigmoidal behaviour for high values of the pressure. V^E is positive for mixtures rich in component 1 and negative for those rich in the second compound. The composition at which the excess volume vanishes moves toward higher molar fractions of component 1 as the pressure is increased. The excess enthalpy exhibits a similar behaviour when the pressure is varied (see figure 1b). The largest change in this magnitude occurs when the pressure moves from a subcritical to a supercritical value. If the pressure is further increased H^E decreases monotonically, although remains positive in the whole range of compositions with the maximum shifted toward high composition values. As can be seen, the theory is able to describe accurately the excess behaviour obtained from simulation in the whole range of compositions and pressures considered here.

The results obtained in figure 1 are not surprising since systems in which the components interact through the Lorentz-Berthelot combining rules can be accurately described using this approach.[39–41] Despite this fact, it is important to remember that no single parameter has been fitted here, and results from the theory correspond to pure predictions. However, is the theory also able to describe so accurately binary mixtures in which the unlike interactions are very asymmetric? To answer this question we have considered two different additional combining rules which can be considered as extreme cases: association and solvation.

We first consider the case of the association combining rules. Figure 2 shows the excess properties obtained from simulation and the van der Waals one-fluid theory corresponding to a binary mixture in which the unlike dispersive interactions are defined through the following relationship: $\epsilon_{12} = \epsilon_{11}$. The unlike segment size follows the Lorentz combining rule, $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$. As can be seen, the excess volume and enthalpy are positive and nearly quadratic in whole range of pressures studied. At low pressures the excess properties exhibit low values, and when the pressure is higher than that corresponding to the critical pressures of both components, the excess properties experiment an enormous variation. Further increase of the pressure produces a decrease of both properties in the whole range of compositions. Agreement between simulation results and theoretical predictions from the van der Waals one-fluid approach is excellent in whole range of thermodynamic conditions considered.

We now study the opposite case, namely, a mixture interacting through the solvation type combining rule in which the unlike dispersive energy parameter is given by $\epsilon_{12} = \epsilon_{22}$. As for the association combining rule this election represents a very asymmetric interaction. Figure 3a represents the excess volume of the mixture obtained from simulation and theory. Contrary to the previous mixtures, excess volume is negative at low pressures and becomes sigmoidal when the pressure is close to the critical value of the mixture. At these conditions, $V^E > 0$ for molar fractions higher than 0.4 approximately, and negative for lower values. As can be seen, the change in magnitude for the excess volume is important and this behaviour can be ascribed to the relative large value of ϵ_{12}. The excess volume is still negative in the whole range of compositions and tends to its ideal value as the pressure is further increased. Figure 3b shows the composition and pressure dependence of the excess enthalpy, which behaves similarly to the excess volume, although an important difference between both thermodynamic properties (excess volume and enthalpy) can be observed: as the pressure is increased the excess volume tends to the ideal behaviour, with the minimum shifted to $x_1 = 0.6$ approximately, while the excess enthalpy decreases its value and remains nearly symmetric as a function of the composition. As can be seen the theory is able to account for the enormous range of variation in the excess property values observed from simulation. Agreement between both results is remarkable taking into account the asymmetry of the mixture and that no single parameter has been fitted.

It is interesting to compare the excess properties of the 2-1 systems with different combining rules. Since the segment size of both components is equal, the excess behaviour is governed by the difference between the pure energy parameters and the unlike interaction value ϵ_{12}. Figure 4 shows the excess volume and enthalpy corresponding to the 2-1 system interacting through the three different combining rules (association, Berthelot and association) at the same thermodynamic conditions. As can be seen (figure 4a), excess volume exhibits positive values when molecules interact through the association combining rule ($\epsilon_{12} = \epsilon_{11} = 84.71$K), sigmoidal behaviour in the case of unlike interactions given by the Berthelot rule ($\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}} = 119.8$K) and negative values for the case of solvation unlike dispersive energy ($\epsilon_{12} = \epsilon_{22} = 169.42$K). This behaviour can be easily interpreted in terms of the unlike dispersive energies since the molecular sizes of both components are equal. In the first case, there is an increase of the volume of mixing due to the unfavorable energy interactions. In the third case, a large value of the unlike dispersive energy produces a strong attractive interactions between components 1 and 2 and consequently, negative values of properties of mixing, and hence negative excess volumes are observed. The system interacting through the Berthelot combining rule represents an intermediate behaviour between the first and third cases. A similar energetic argument can be used to explain the features exhibited by the excess enthalpy, as shown in figure 4b. The association combining rule produces the largest value of the excess enthalpy, while the solvation rule gives negative values of the excess enthalpy. As for the excess volume, the unlike dispersive energy value given by the Berthelot combining rule produces an intermediate behaviour of the excess enthalpy.

4.2 2-2 systems

We consider now systems in which the dispersive energy and segment size ratios are equal to 2, i. e., $\sigma_{22}/\sigma_{11})^3 = 2$ and $\epsilon_{22}/\epsilon_1 = 2$. As in the previous section we study the effect of the pressure on the excess functions when different combining rules corresponding to the unlike dispersive energy are used.

Figure 5 shows the excess volume and enthalpy corresponding to the system in which the unlike interactions are described via the Lorentz-Berthelot combining rules. As can be seen in figure 5a, the excess volume exhibits high positive values and a nearly quadratic shape shifted toward low concentration values at low pressures. As the pressure of the mixture approaches to $p = 100$atm the excess volume behaves as a sigmoidal curve ($V^E > 0$ for high x_1 values and $V^E < 0$ for low molar fractions), and at $p > 100$atm it exhibits negative values in the whole range of compositions. The excess enthalpy (see figure 5b) behaves in a similar way, i. e., positive values at low pressures, negative values at high pressures, and sigmoidal behaviour at intermediate values of the pressure. As can be observed it exists a range of intermediate pressures, between 200 and 400atm, in which the excess enthalpy behaves as a sigmoidal curve while the excess volume is negative in the whole range of compositions. Agreement between simulation results and theoretical predictions is excellent in all cases. It is interesting to note that the agreement between both results is better in the 2-2 systems than in the 2-1 systems. This prediction indicates that the van der Waals one-fluid approach is able to describe more accurately systems in which the segment size and dispersive energy ratios are correlated: it is expected that a larger molecular size is associated to a larger dispersive interaction energy. This is consistent with the molecular parameter values of the intermolecular potentials used to describe the thermodynamic behaviour of real systems.

Similarly to the case of the 2-1 systems, we have also considered two additional combining rules, the association and solvation combining rules, to study the effect of different values of the parameter ϵ_{12} on the excess volume and enthalpy. Results corresponding to the excess volume and enthalpy for mixtures interacting through the association combining rule are shown in figure 6. The excess volume exhibits relative large values at low pressures ($p \leq 100$atm), and becomes a sigmoidal function of composition, with low excess volumes at higher pressures. V^E is positive for mixtures rich in the first component and $V^E < 0$ for those rich in the second component. The excess enthalpy shows low values at $p = 30$atm, high values at $p = 100$atm and intermediate positive values at higher pressures. Contrary to the excess volume, H^E is always positive in the whole range of compositions. Agreement between simulation results and theoretical predictions is remarkable in all cases. The excess volumes and enthalpies corresponding to the S-2-2 binary mixtures exhibit a more complex behaviour when the pressure is varied. As can be seen in figure 7a, V^E is negative at all pressures considered, except at $p = 60$ and 100atm. At the first pressure, V^E is positive in the whole range of compositions, and for $p = 100$atm the excess volume exhibits a very asymmetric sigmoidal shape, with the minimum shifted toward low composition value and the maximum being close to $x_1 = 1$. The excess enthalpy shows a similar behaviour as the pressure is increased, passing from nearly ideal mixture behaviour ($p = 30$atm), positive ($p = 60$atm), sigmoidal shape ($p = 100$atm) and negative values at higher pressures. As can be seen, the van der Waals one-fluid theory is able to predict correctly the asymmetric excess behaviour of the S-2-2 systems at all thermodynamic conditions.

As for the 2-1 binary mixtures, we have explicitly studied the effect of the combining rules on the excess volume and enthalpy for the 2-2 systems and results are presented in figure 8. The excess volume behaviour (and also the excess enthalpy) can be understood from its molecular properties in the case of simple fluids which have spherical shape and have no specific interactions, such as association. From a very simplified point of view, one can says that a positive excess volume implies an expansion of the volume mixture (with respect to that of the pure components) due to unfavourable or repulsive interactions; a negative V^E corresponds to a contraction of the mixture volume due to favourable attractive interactions. Under this perspective, the excess volume of the 2-2 systems is governed by the value of the unlike dispersive interaction parameter ϵ_{12}. Figure 8a shows the excess volume for the 2-2 systems using different values of ϵ_{12} (or equivalently, different combining rules for the unlike dispersive energy parameter): 119.8K (Berthelot), 84.71K (association) and 169.42K (solvation). As in the previous case (the 2-1 systems), the excess volume exhibits the highest values when ϵ_{12} is given by the association combining rule, the lowest values for the case of the solvation, and intermediate values when the mixture components interact through the Berthelot rule. This behaviour, as previously stated, is a direct consequence of the favourable/unfavourable energetic interactions. Figure 8b shows the results obtained for the excess enthalpy. As can be seen, a similar behaviour is obtained when the unlike dispersive energy is changed from the association through the Berthelot to the solvation combining rule. It is interesting to compare the results obtained for the 2-2 systems with those corresponding to the 2-1 binary mixtures. Both results are qualitatively similar but in the present case all excess values are shifted toward more negative values. This is related with the different value of the segment size ratio of the two sets of systems. As can be observed, the van der Waals one-fluid theory is able to describe correctly the effect of changing ϵ_{12} in both excess properties.

4.3 2-1/2 systems

In the previous two sections we have considered binary mixtures in which the dispersive energy ratio is equal to two ($\epsilon_{22}/\epsilon_{11} = 2$) and the segment size of substances considered are equal or the segment size of the second component is larger than that corresponding to the first one, which seems to be a reasonable set of parameters for describing real systems. Here we now consider rather unrealistic systems in which the dispersive energy ration is equal to 2 and the segment size ratio is given by $(\sigma_{22}/\sigma_{11})^3 = 1/2$. This class of system represents a binary mixture in which the smaller component has twice the dispersive interaction energy than the bigger substance. Although this is a very unrealistic situation, we consider this system to check the capability of the van der Waals one-fluid theory in predicting the excess properties of such an asymmetric binary mixture.

Figure 9 shows the excess volume and enthalpy obtained from simulation and theory. As can be seen, the simulation and theoretical predictions yield positive values for both excess properties in the whole range of compositions and pressures. However, although the theory is able to predict the general trends of the simulation data in the whole range of pressure conditions, it overestimates the simulation results at all the pressures considered. It is important to take into account that the theoretical results are pure predictions and the systems considered here constitute very unrealistic mixtures.

As in the previous section, we have also explicitly compared the excess properties of the 2-(1/2) binary mixtures when different combining rules for the dispersive energy are used. In figure 10 we show how the excess volume and enthalpy for these systems change as the combining rule for ϵ_{12} is changed: both excess functions decrease as the combining rules are changed from the association, through the Berthelot to the solvation combining rules, which is also a direct consequence of the increasing of the dispersive energy when passing through the different combining rules used. These results is qualitatively the same as those found for the 2-1 and 2-2 systems but with a difference: now, the excess function values are shifted toward higher values. This is due to the difference in size of the components forming the 2-(1/2) binary mixtures.

4.4 Temperature dependence of the excess properties

In the previous sections we have studied the dependence of the excess functions (volume and enthalpy) on the composition and pressure, at constant temperature. Now we consider the temperature dependence of the excess volume and enthalpy for selected systems.

Figure 11 shows the excess volume and enthalpy corresponding to the LB-2-1 binary mixtures at three different temperatures and two pressures. As can be seen, excess volume and enthalpy exhibit a strong dependence with temperature, which is more evident when the system is at near critical pressures ($p = 100$atm). In this case, the main effect of increasing the temperature is to shift the excess curves toward its ideal values. However, for supercritical pressures ($p = 300$atm), the excess volume and enthalpy are kept approximately constant in the whole range of compositions. We have also considered the same type of system, the 2-1 mixtures, but now the unlike interaction parameters are given by the association combining rules (A-2-1). As can been seen in figure 12, a more complicate behaviour is exhibited by this system: at low pressures, an increase of the temperature produces a decrease of the excess volume, while at high pressures the excess volume increases as the temperature is raised (figure 12a); the excess enthalpy, at the two different pressures considered, decreases in the whole range of compositions when the temperature is increased.

We also consider the effect of temperature on the excess properties for the 2-2 systems. Figure 13 shows the excess functions for the LB-2-2 binary mixtures. The main effect of increasing the temperature of the system is to increase the excess properties when the pressure is near the critical pressures of both components, and to decrease the excess volume and enthalpy as the temperature is increased.

Finally, we have studied the excess properties of the S-2-2 binary mixtures at two pressures and three different temperatures, and results are shown in figure 14. The behaviour exhibited by both excess functions is much simpler at supercritical pressures, far away from the critical pressure at which an increase of the temperature shifts the excess curves to higher values. However, the behaviour exhibited by the excess volume and enthalpy is much complicated at near critical pressures: both properties behave as sigmoidal functions of composition at 230 and 250K, but become negative in the whole range of compositions when the temperature is raised to 300K. This complex behaviour is a direct consequence of the asymmetry of the mixture, as well as a characteristic of the near critical fluid state.

5 Conclusion

NpT Monte Carlo simulations have been performed to obtain the excess thermodynamic properties of binary mixtures of spherical Lennard-Jones molecules. The influence of several molecular parameters and thermodynamic conditions on the excess functions of these systems have been discussed in detail. The results obtained from molecular simulation have been used to check the accuracy of the simplest conformal solution theory, i .e., the van der Waals one-fluid theory in predicting this kind of thermodynamic properties.

We have studied the influence of the segment size and dispersive energy ratios of pure components, as well as the use of different combining rules corresponding to the unlike dispersive energy parameter, on the excess properties of Lennard-Jones systems. In addition, we have also considered the effect of pressure and temperature on the excess volume and enthalpy. The excess functions exhibit low absolute values for the excess volume and enthalpy in the whole range of compositions below the critical point. However, V^E and H^E show a complicate behaviour in the supercritical region for all the systems considered, including positive and negative values, complex concentration dependence, and large pressure and temperature dependence. This complex non-ideal behaviour observed is a direct consequence of the volumetric behaviour of the system in the supercritical region.

In order to check the accuracy of the van der Waals one-fluid theory, we have compared the simulation data and theoretical predictions without fitting any molecular parameter. Comparison between simulation and theory indicate that the van der Waals one-fluid theory is able to predict correctly the excess behaviour of binary mixtures of spherical Lennard-Jones molecules. In particular, the predictions from the theory are in excellent agreement with simulation for X-2-1 and X-2-2 binary mixtures using different combining rules, including some asymmetric mixtures which can be named as extreme cases. The results corresponding to the X-2-(1/2) systems indicate that the van der Waals one-fluid theory is able to predict qualitatively the complex behaviour exhibited by the excess properties of such mixtures. This is an important result since theoretical results are obtained as pure predictions and this kind of systems can be considered rather unrealistic.

Results obtained in this work clearly indicate the ability of the van der Waals one-fluid theory in predicting the excess thermodynamic behaviour of asymmetric binary mixtures of spherical molecules. This is especially relevant when this theoretical approach is used to account for the thermodynamic properties of a reference fluid in more sophisticated perturbation theories. This is the case of the SAFT approach in which a spherical reference fluid is needed to predict the thermodynamic behaviour of complex binary mixtures, such as those formed by chainlike and/or associating molecules.

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Table 1. Intermolecular potential parameters for pure components corresponding to the three different mixtures studied. See the text for further details.

		σ(nm)		
	ϵ/k_B(K)	X-2-(1/2)	X-2-1	X-2-2
Component 1	84.71	0.3797	0.3405	0.3013
Component 2	169.42	0.3013	0.3405	0.3797

Table 2. Critical temperatures and pressures for pure components.

System	Component	T_c(K)	p_c(MPa)
	1	108	3.546
X-2-1	2	216	6.991
	1	108	5.066
X-2-2	2	216	5.066
	1	108	2.533
X-2-(1/2)	2	216	10.133

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Figure 1. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to LB-2-1 systems at $T = 230$K. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 1$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike interaction parameters are given by the Lorentz-Berthelot combining rules. The continuous curves correspond to the predictions from the van der Waals one-fluid theory and the symbols represent the NpT MC simulation results at $p = 30$ (circles), 60 (squares), 100 (diamonds), 200 (triangles up), 300 (triangles left), 400 (triangles down) and 500atm (triangles right).

Figure 2. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to A-2-1 systems at $T = 230$K. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 1$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike segment size and dispersive energy parameter is given by $\epsilon_{12} = \epsilon_{11}$ (association combining rule). The continuous curves correspond to the predictions from the van der Waals one-fluid theory and the symbols represent the NpT MC simulation results at $p = 30$ (open circles), 60 (squares), 100 (diamonds), 200 (triangles up), 300 (triangles left), 400 (triangles down), 500 (triangles right), 600 (plus), 700 (crosses), 800 (stars) and 1000atm (filled circles).

Figure 3. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to S-2-1 systems at $T = 230$K. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 1$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike segment size is given by the Lorentz combining rule and $\epsilon_{12} = \epsilon_{22}$ (solvation combining rule). Legends are the same as in the previous figure.

Figure 4. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules at $T = 230$K and $p = 300$atm. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 1$ and $\epsilon_{22}/\epsilon_{11} = 2$. The continuous curves correspond to the predictions from the van der Waals one-fluid theory and the symbols represent the

NpT MC simulation results for A-2-1 systems (circles), LB-2-1 systems (squares) and S-2-1 systems (diamonds).

Figure 5. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to LB-2-2 systems at $T = 230$K. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 2$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike interaction parameters are given by the Lorentz-Berthelot combining rules. Legends are the same as in figure 2.

Figure 6. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to A-2-2 systems at $T = 230$K. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 2$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike segment size is given by the Lorentz combining rule and $\epsilon_{12} = \epsilon_{11}$ (association combining rule). Legends are thesame as in figure 2.

Figure 7. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to S-2-2 systems at $T = 230$K. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 2$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike segment size is given by the Lorentz combining rule and $\epsilon_{12} = \epsilon_{22}$ (solvation combining rule). Legends are the same as in figure 2.

Figure 8. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules at $T = 230$K and $p = 300$atm. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 2$ and $\epsilon_{22}/\epsilon_{11} = 2$. Legends are the same as in figure 4.

Figure 9. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to LB-2-(1/2) systems at $T = 230$K. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 1/2$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike interaction parameters are given by the Lorentz-Berthelot combining rules. Legends are

the same as in figure 2.

Figure 10. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules at $T = 230\mathrm{K}$ and $p = 300\mathrm{atm}$. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 1/2$ and $\epsilon_{22}/\epsilon_{11} = 2$. Legends are the same as in figure 4.

Figure 11. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to LB-2-1 systems. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 1$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike interaction parameters are given by the Lorentz-Berthelot combining rules. The continuous and dashed curves correspond to the predictions from the van der Waals one-fluid theory at $p = 100$ and 300atm, respectively, and the open and filled symbols represent the NpT MC simulation results at $p = 100$ and 300atm, respectively, and $T = 230$ (circles), 250 (squares) and 300K (diamonds).

Figure 12. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to A-2-1 systems. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 1$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike segment size is given by the Lorentz combining rule and $\epsilon_{12} = \epsilon_{11}$ (association combining rule). Legends are the same as in the previous figure.

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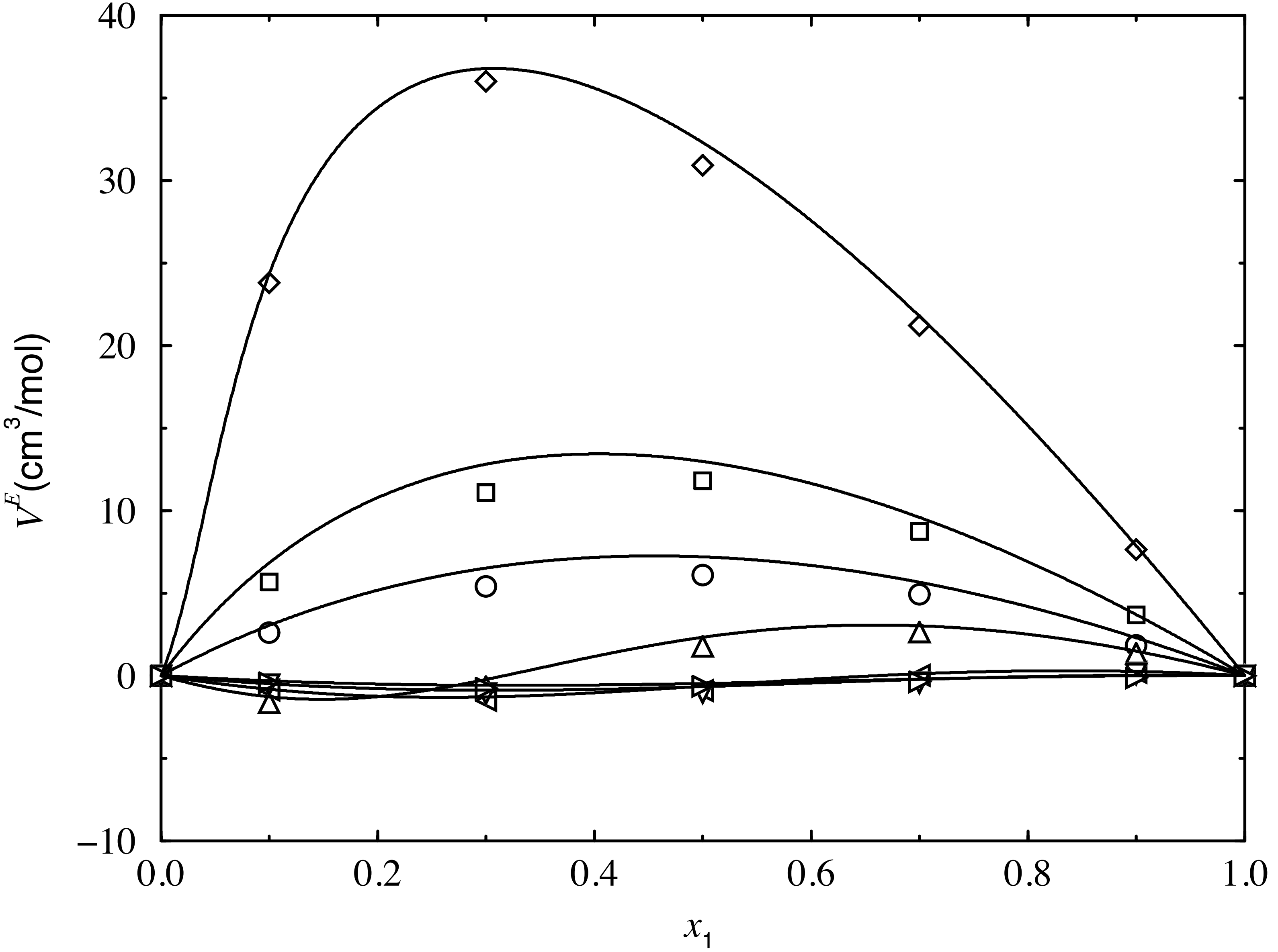
Figure 14. Excess volume (a) and enthalpy (b) of binary mixtures of spherical Lennard-Jones molecules corresponding to S-2-2 systems. The segment size and dispersive energy ratios are given by $(\sigma_{22}/\sigma_{11})^3 = 2$ and $\epsilon_{22}/\epsilon_{11} = 2$. The unlike segment size is given by the

Lorentz combining rule and $\epsilon_{12} = \epsilon_{22}$ (solvation combining rule). Legends are the same as in figure 11.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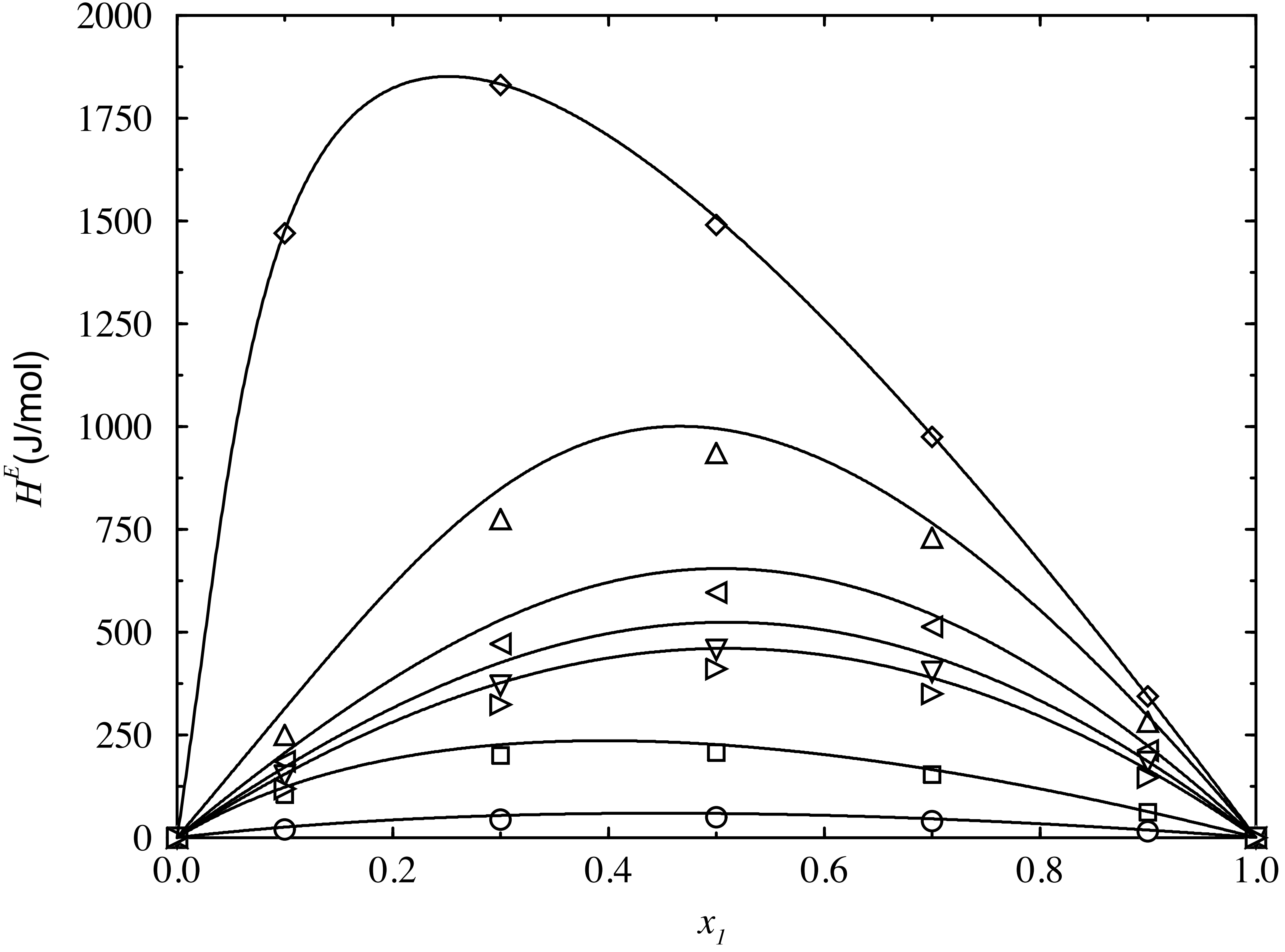
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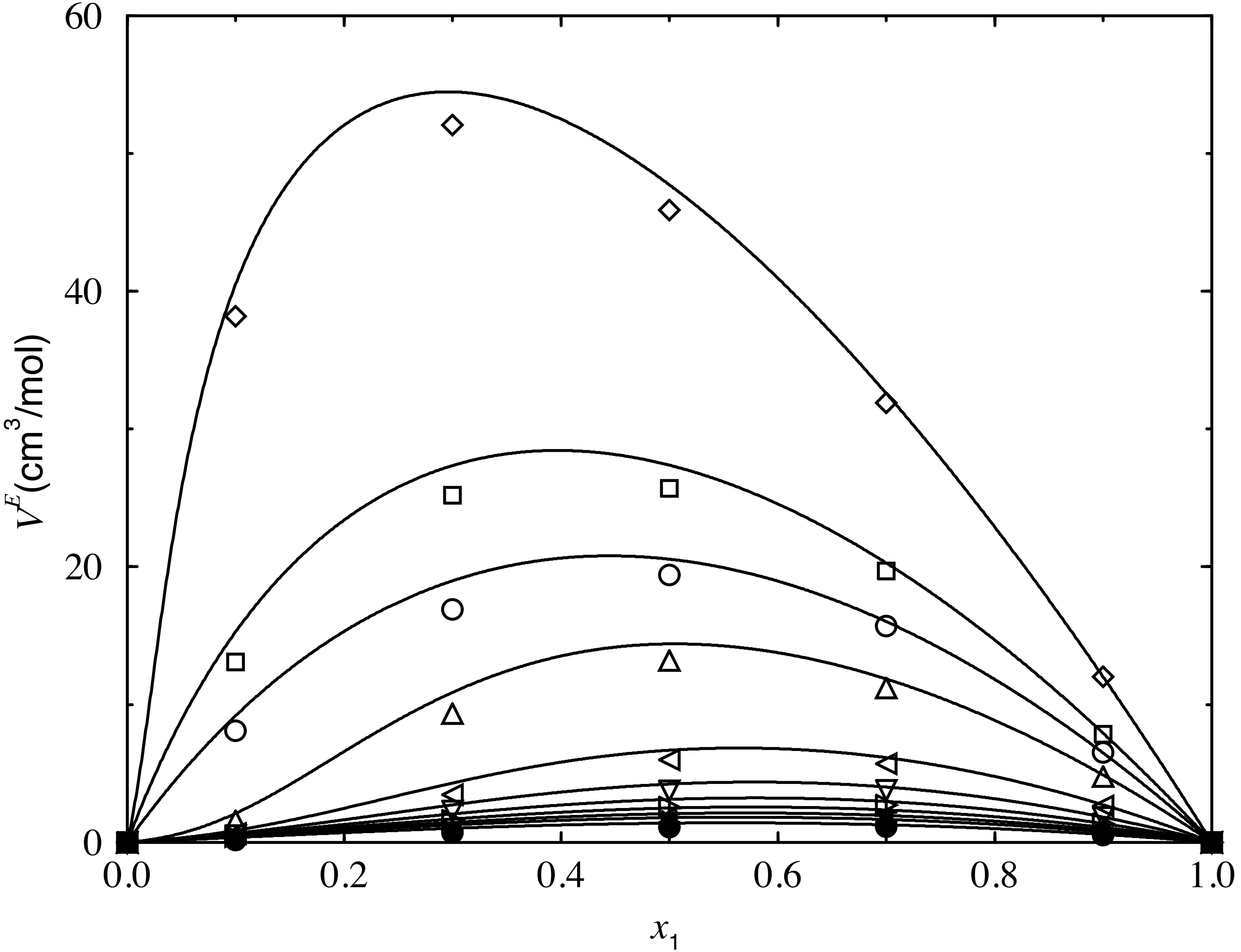

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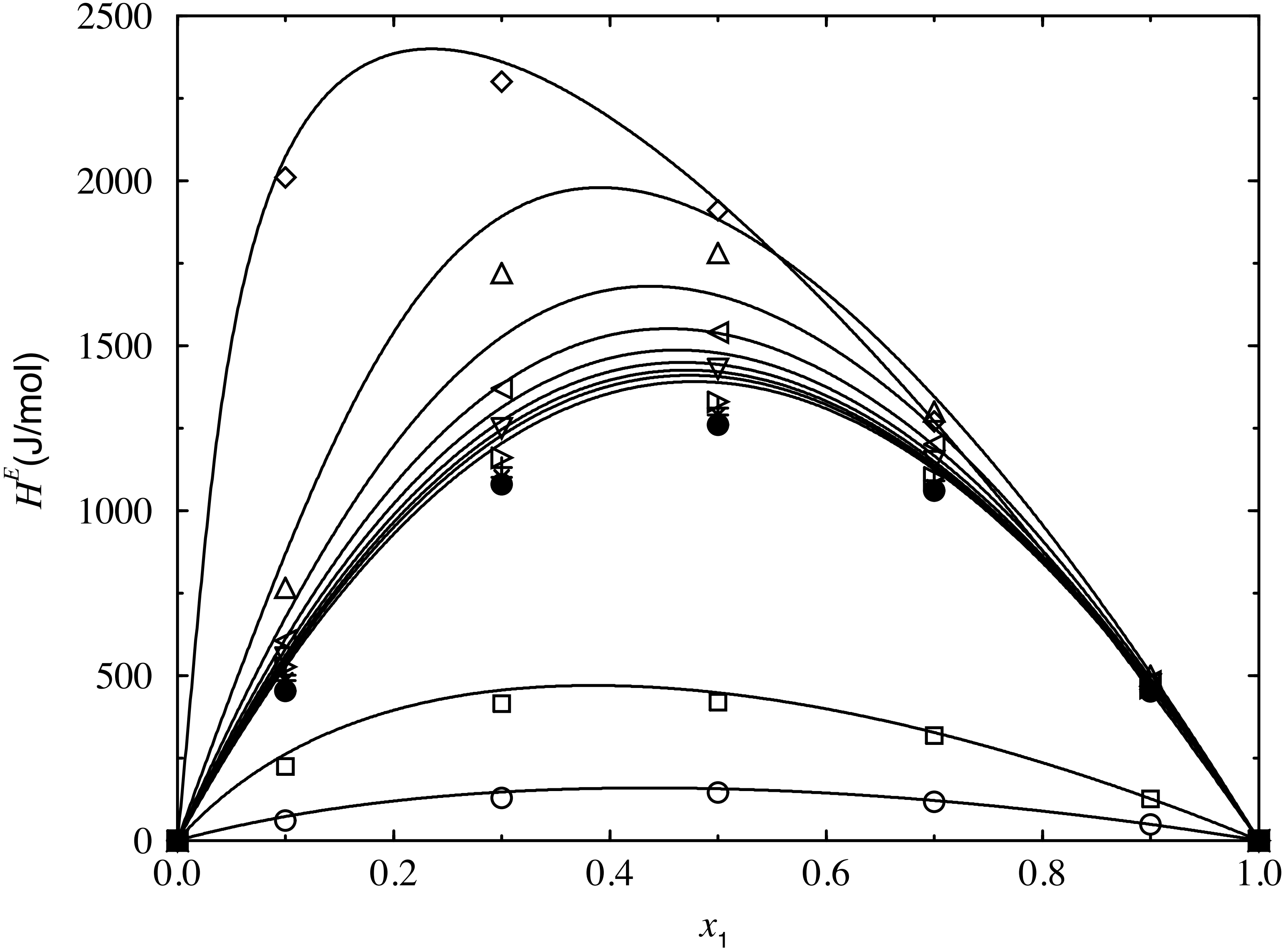

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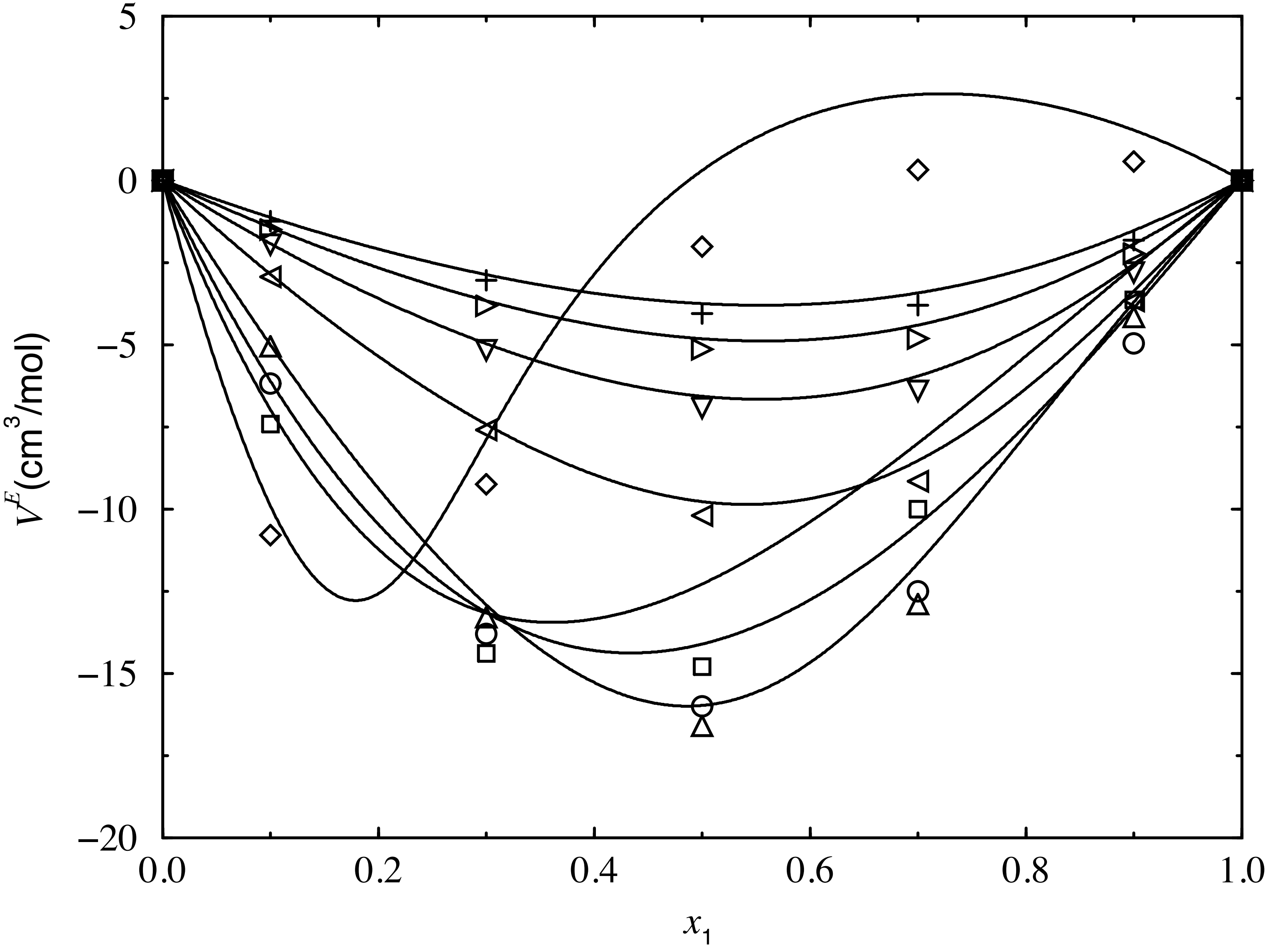
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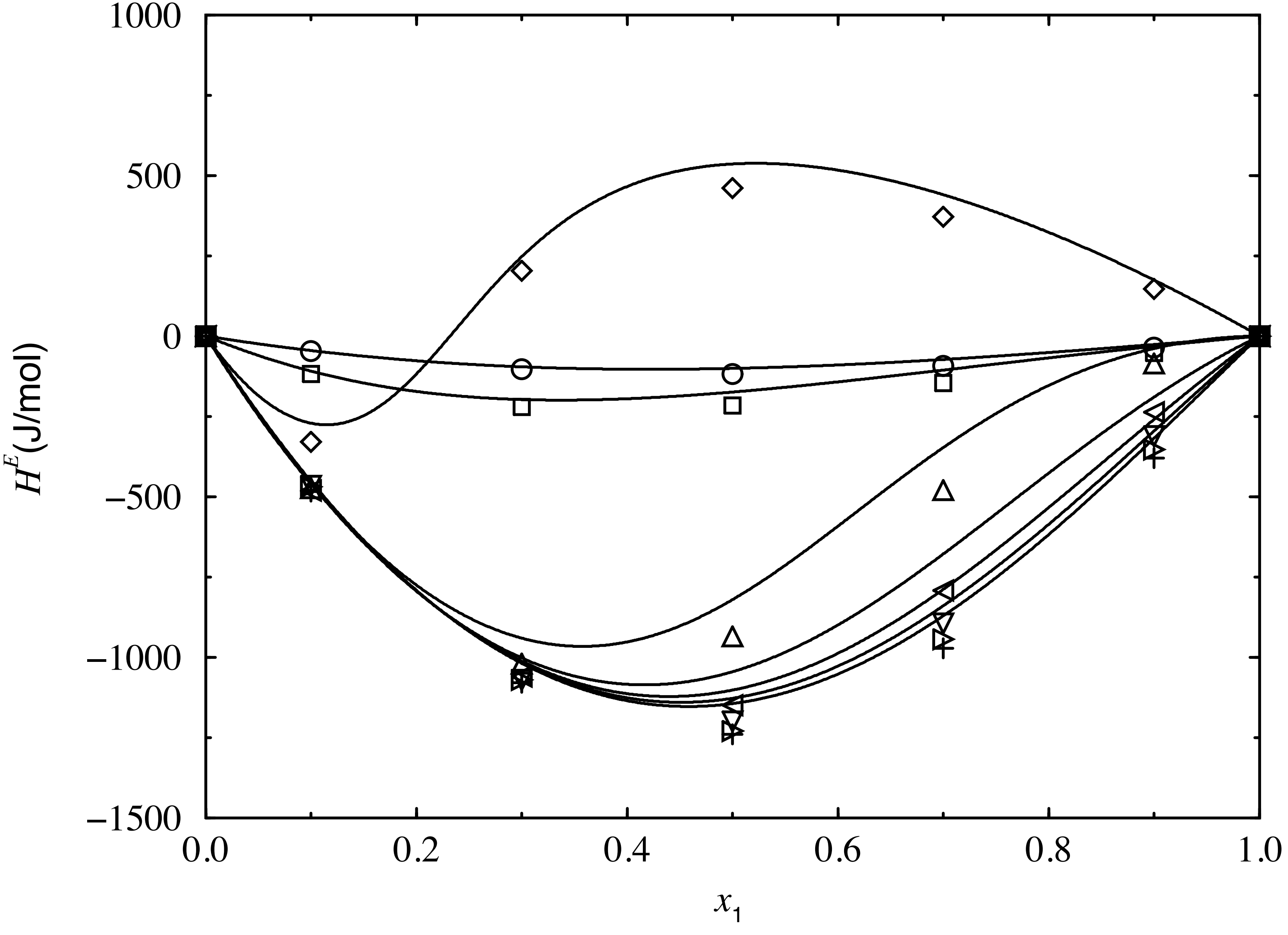

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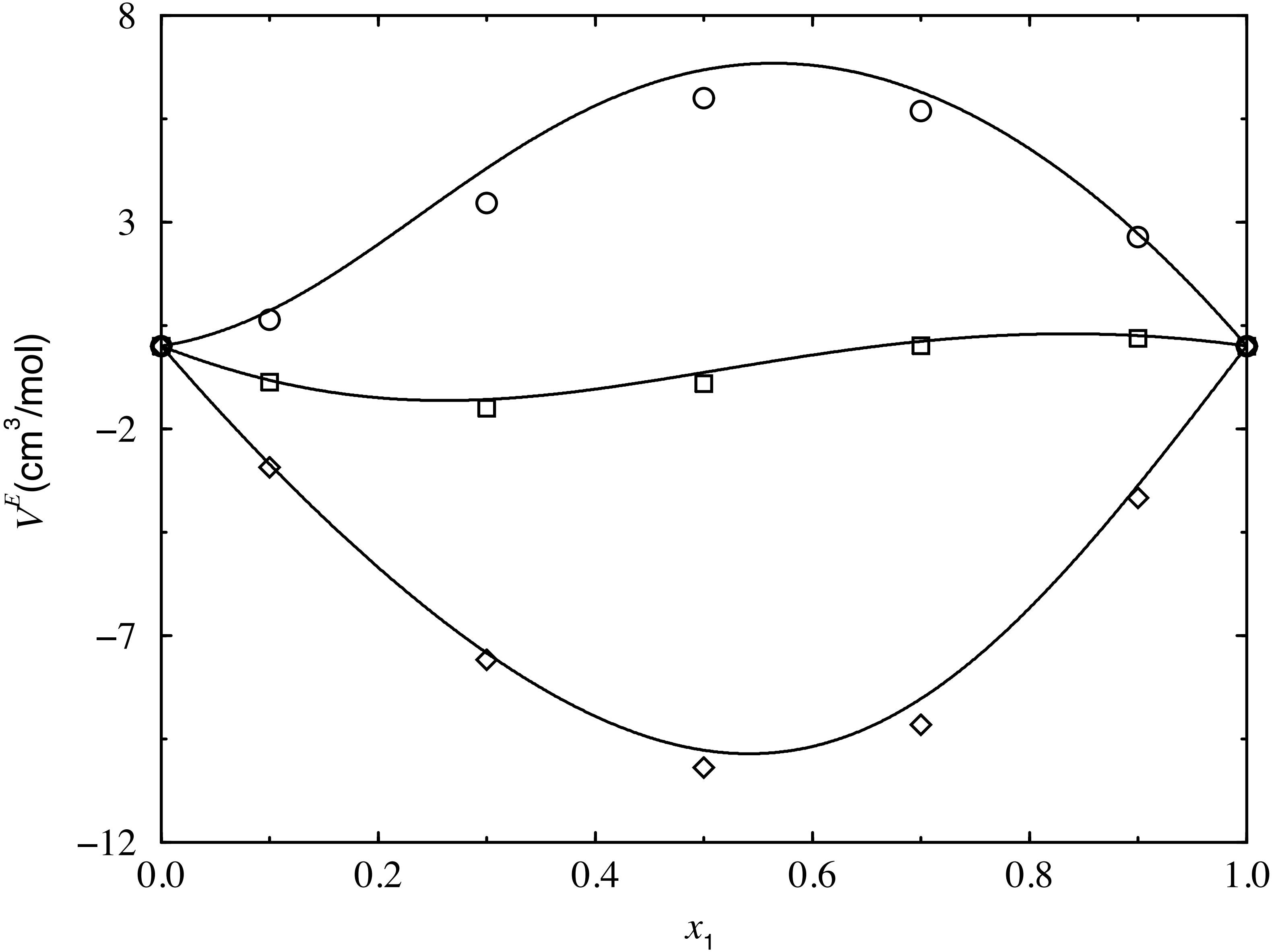
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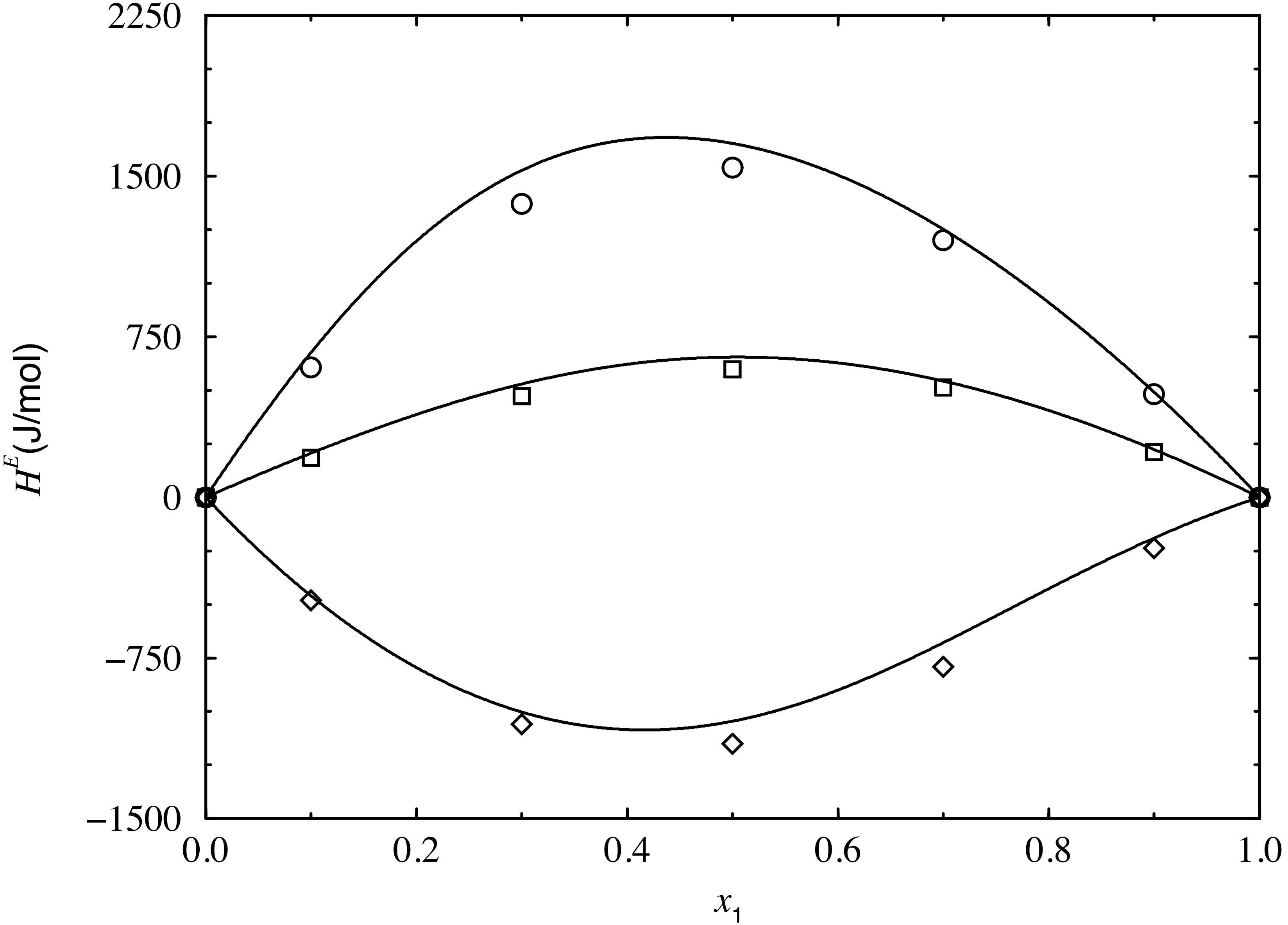
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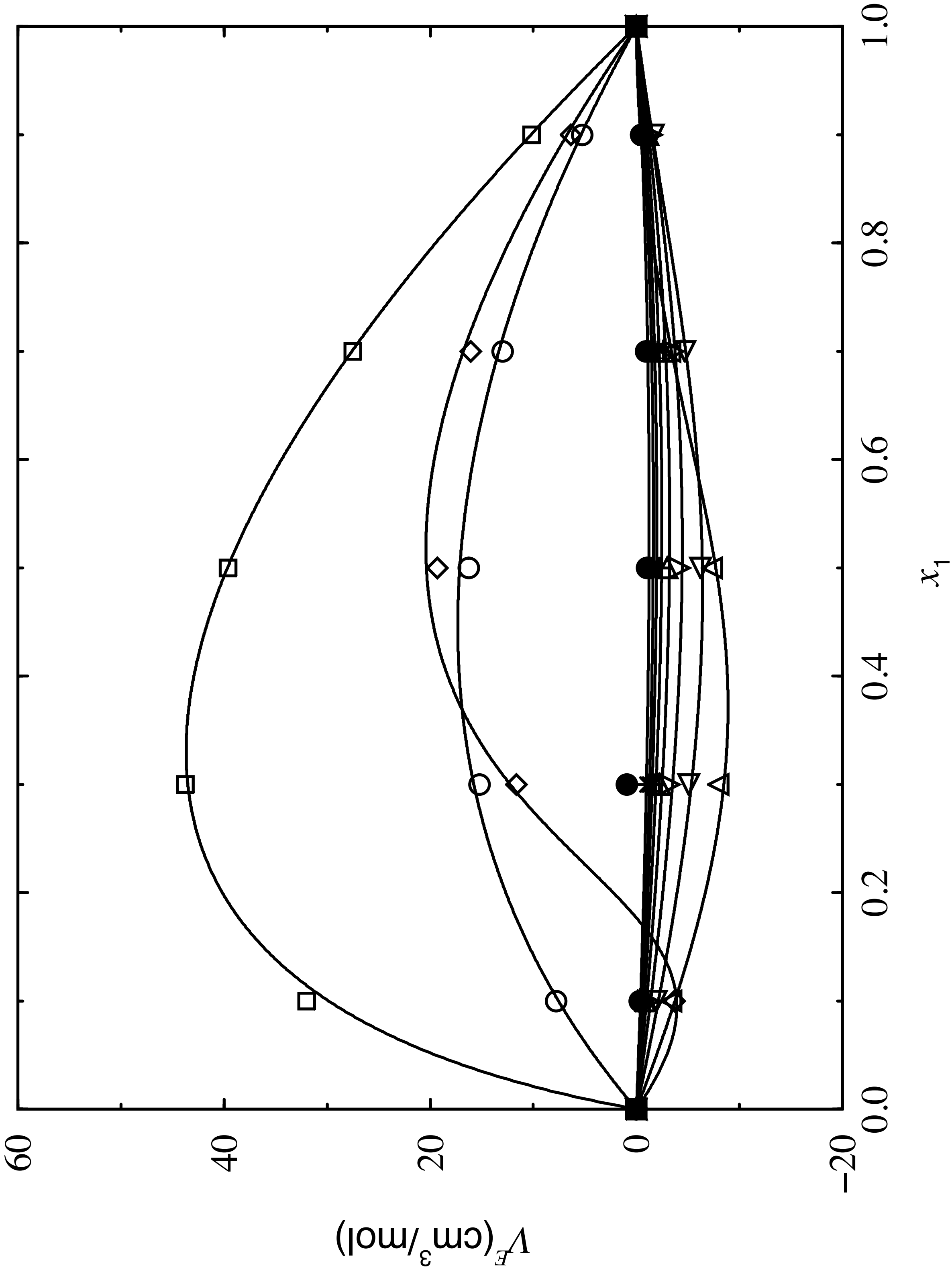
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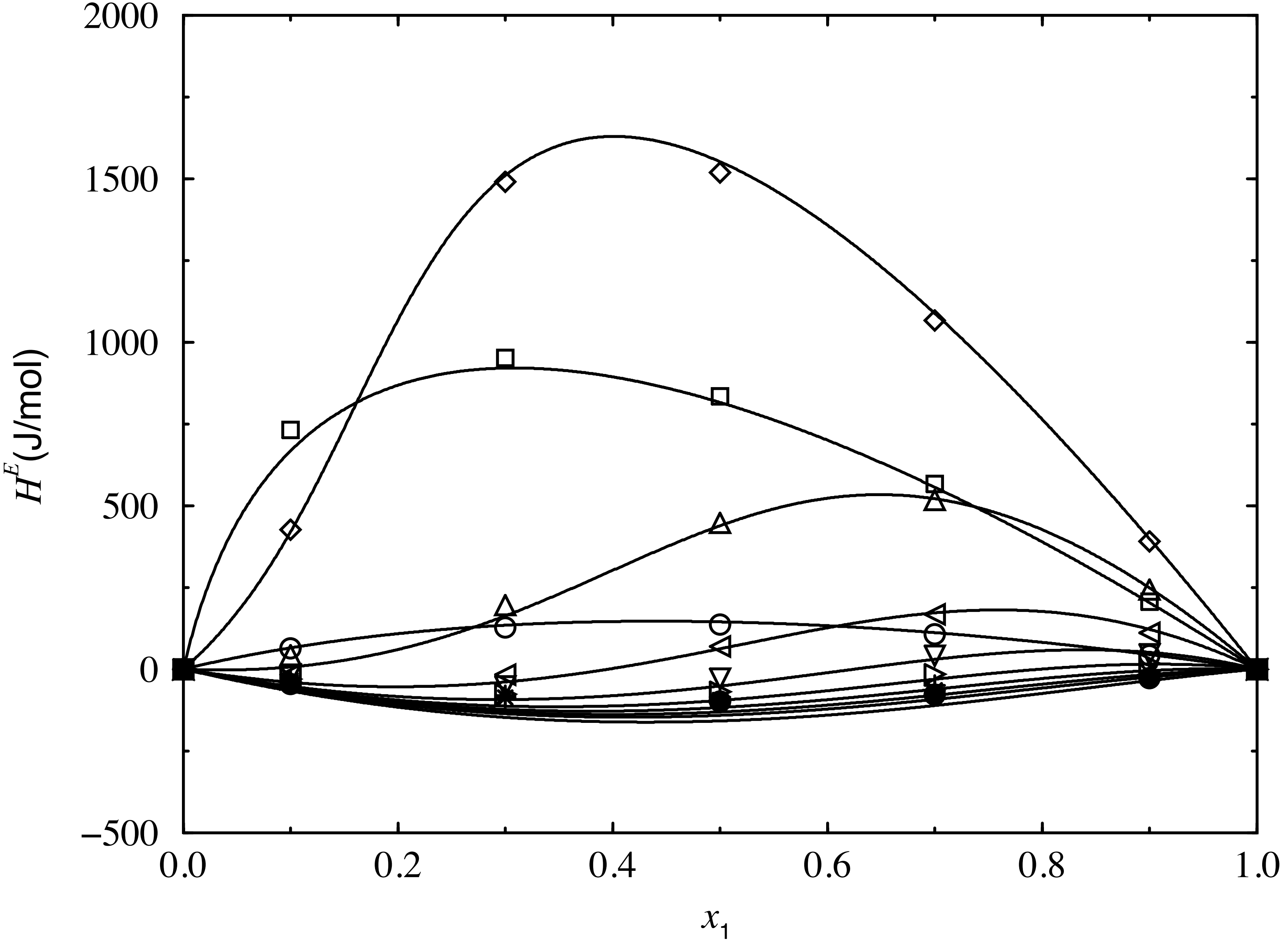
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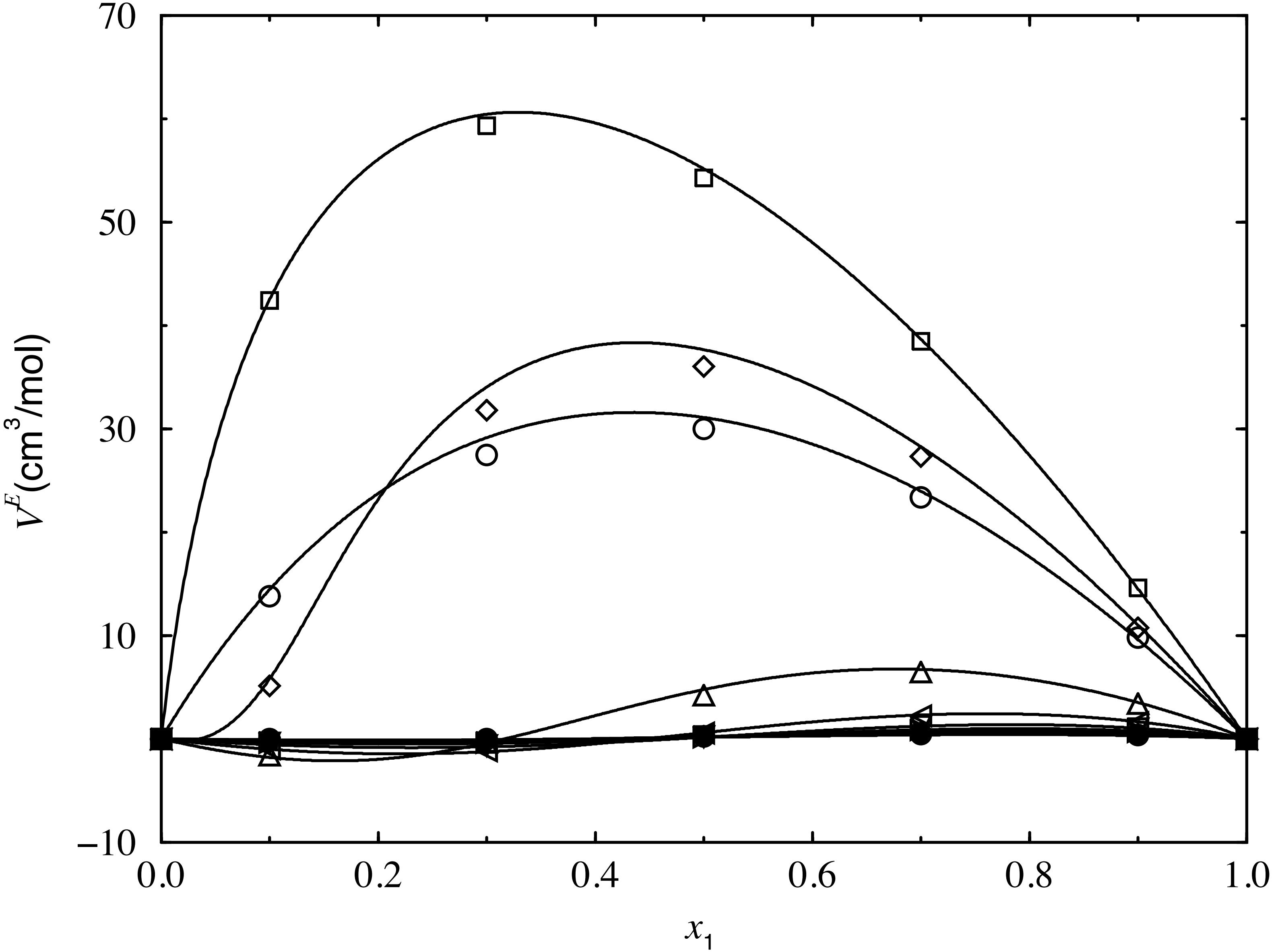
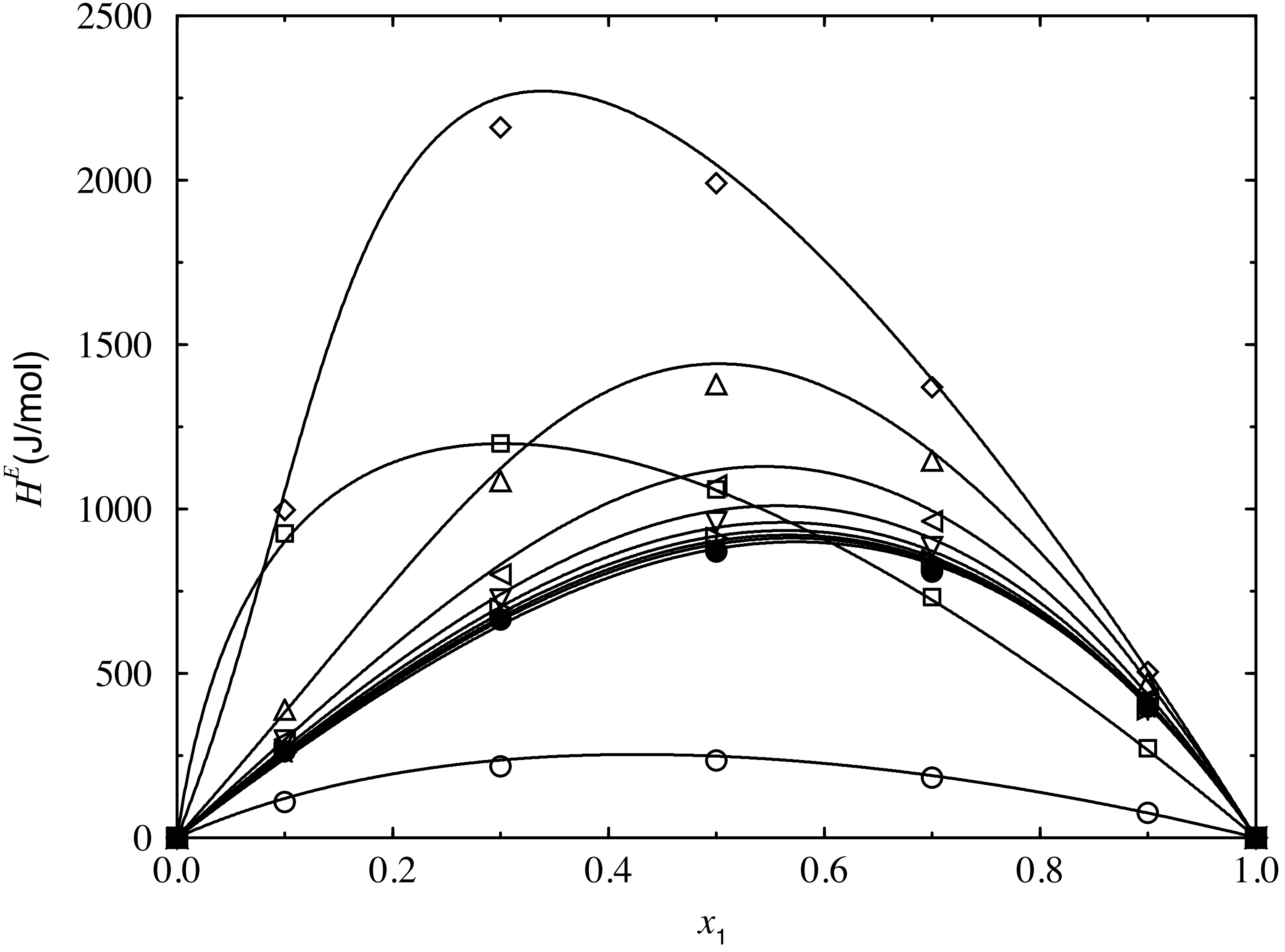
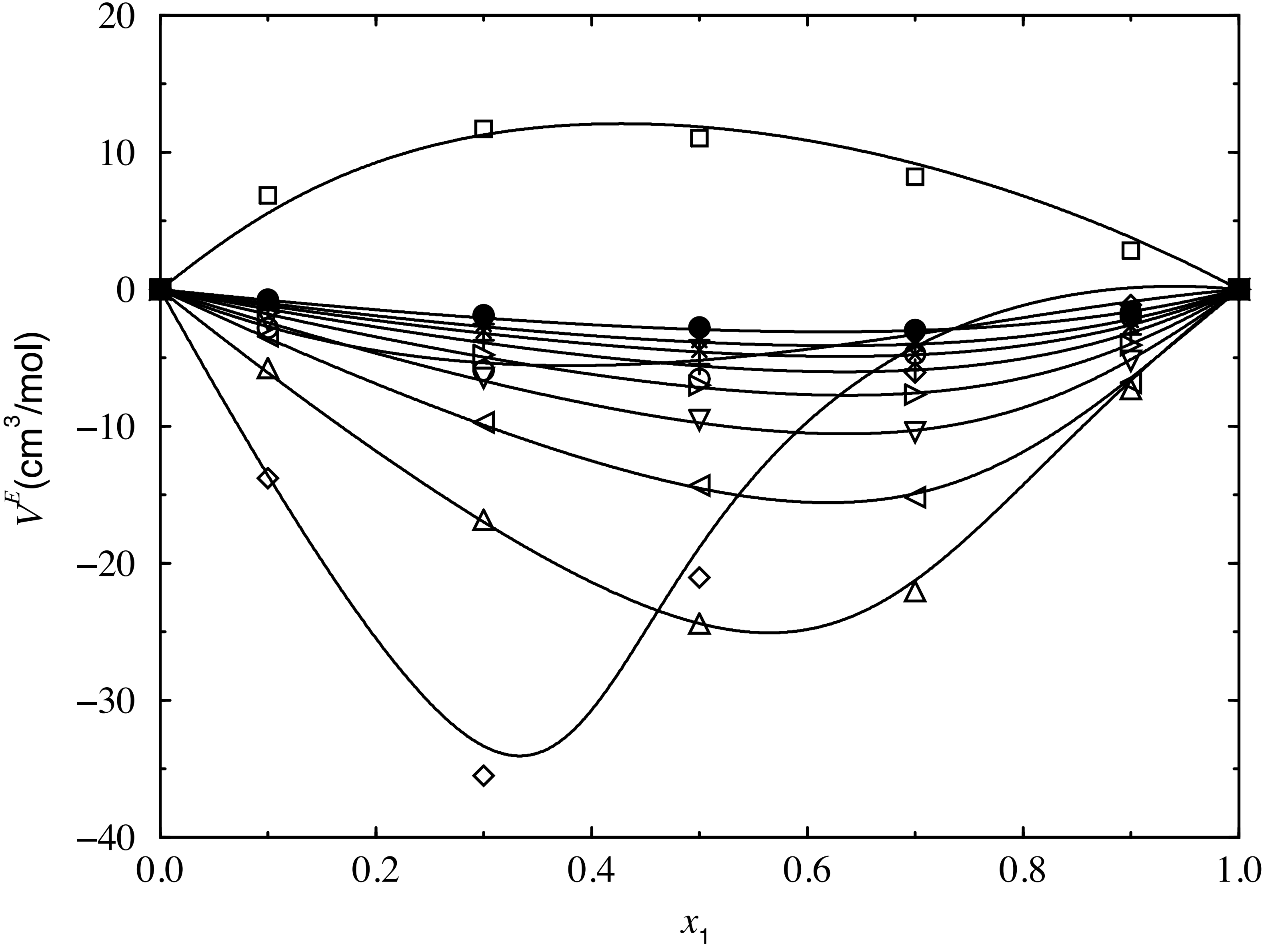
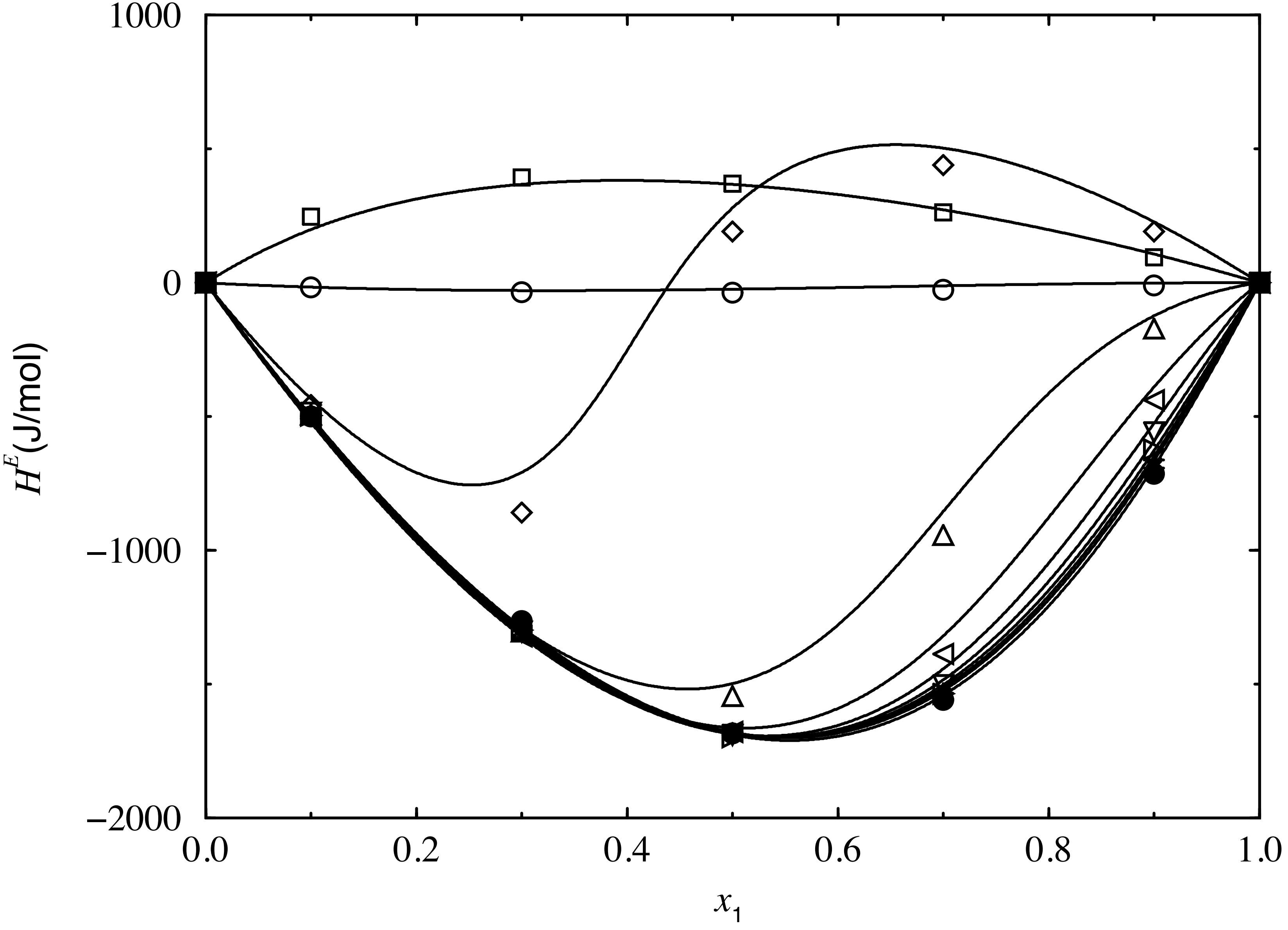
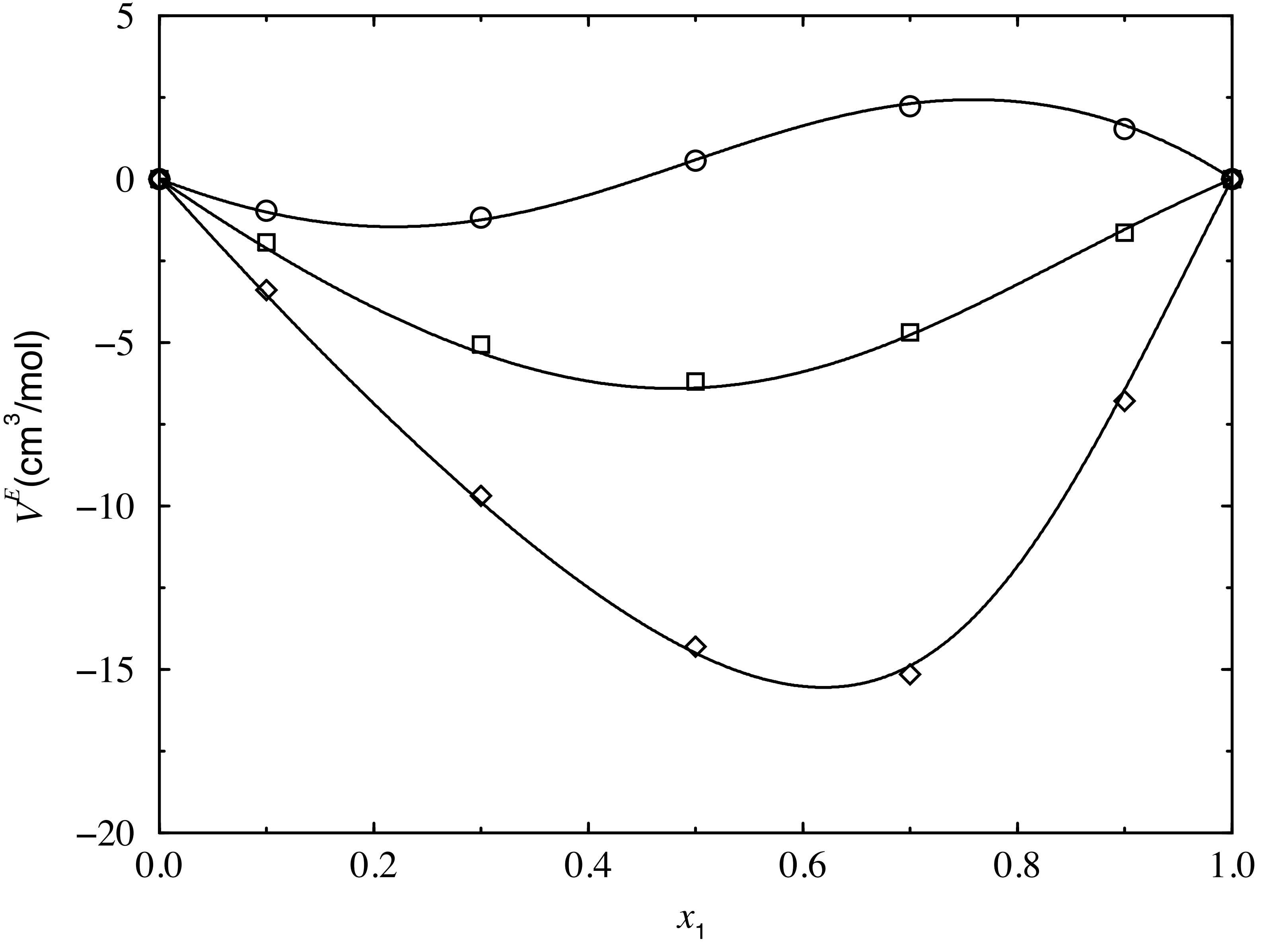
1.0
x_1

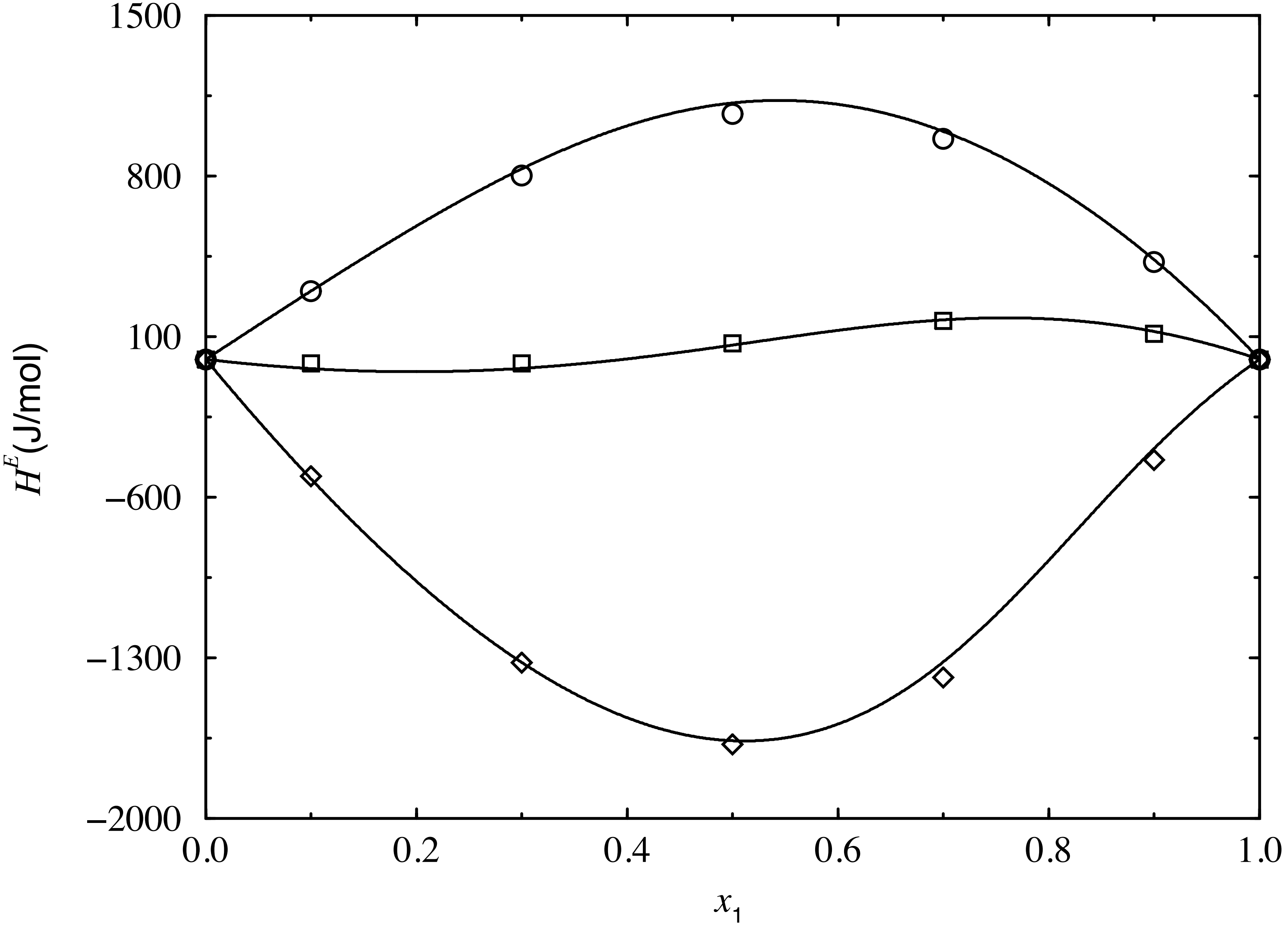

70
50
30
10
−10
V^E(cm^3/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1

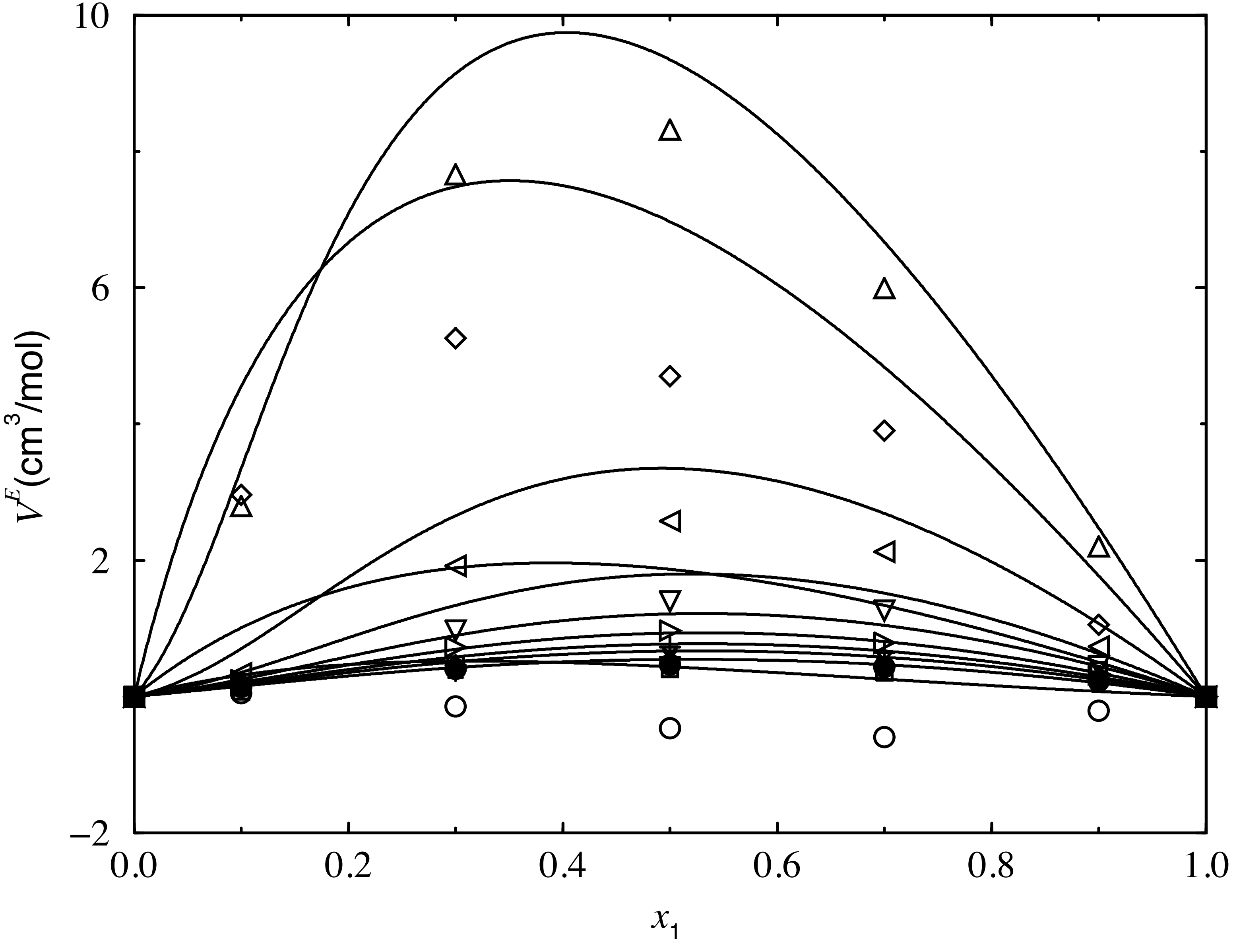

2500
2000
1500
1000
500
0
H^E(J/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1

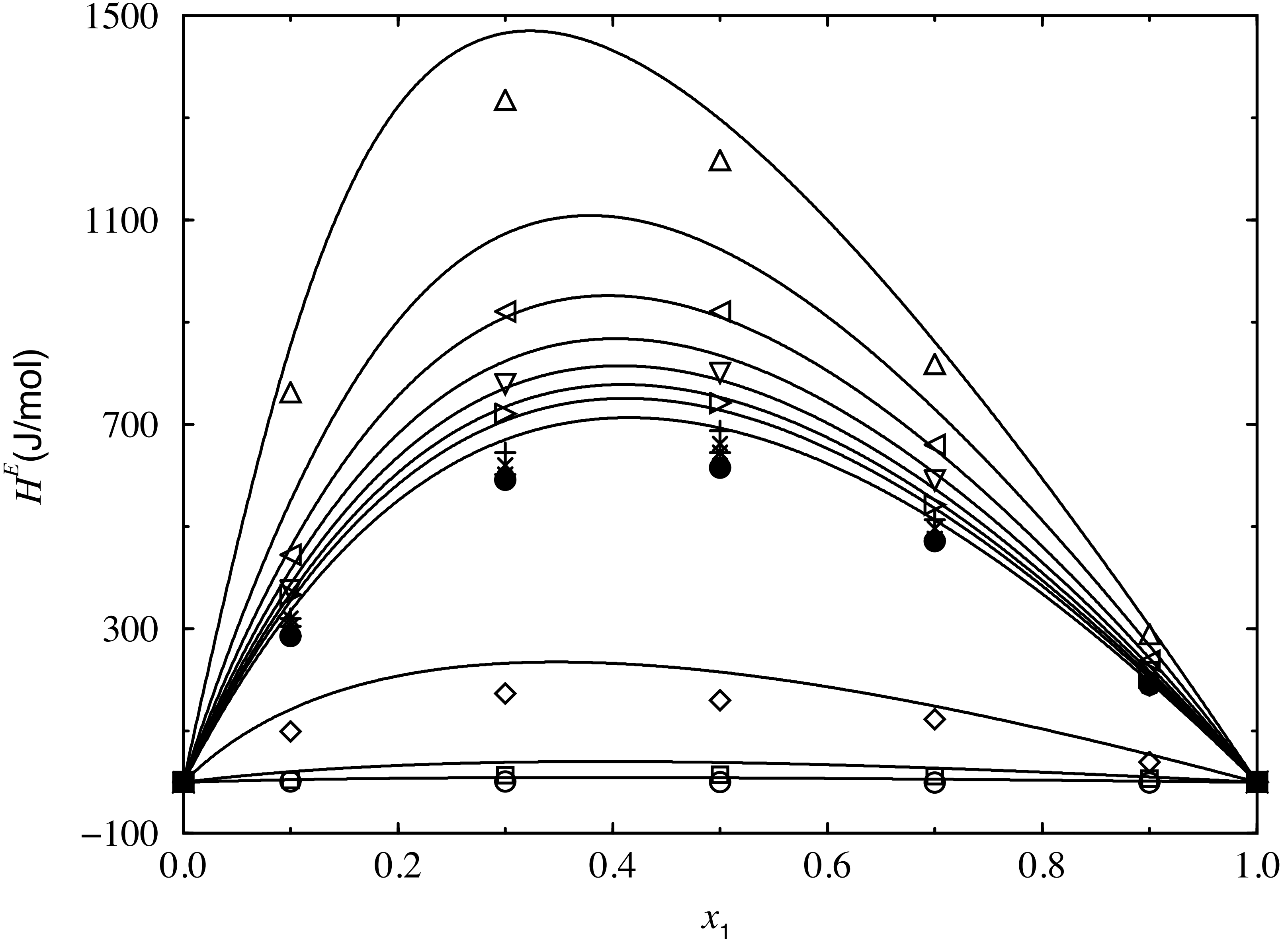

20
10
0
−10
−20
−30
−40
0.0
0.2
0.4
0.6
0.8
1.0
V^E(cm^3/mol)
x_1

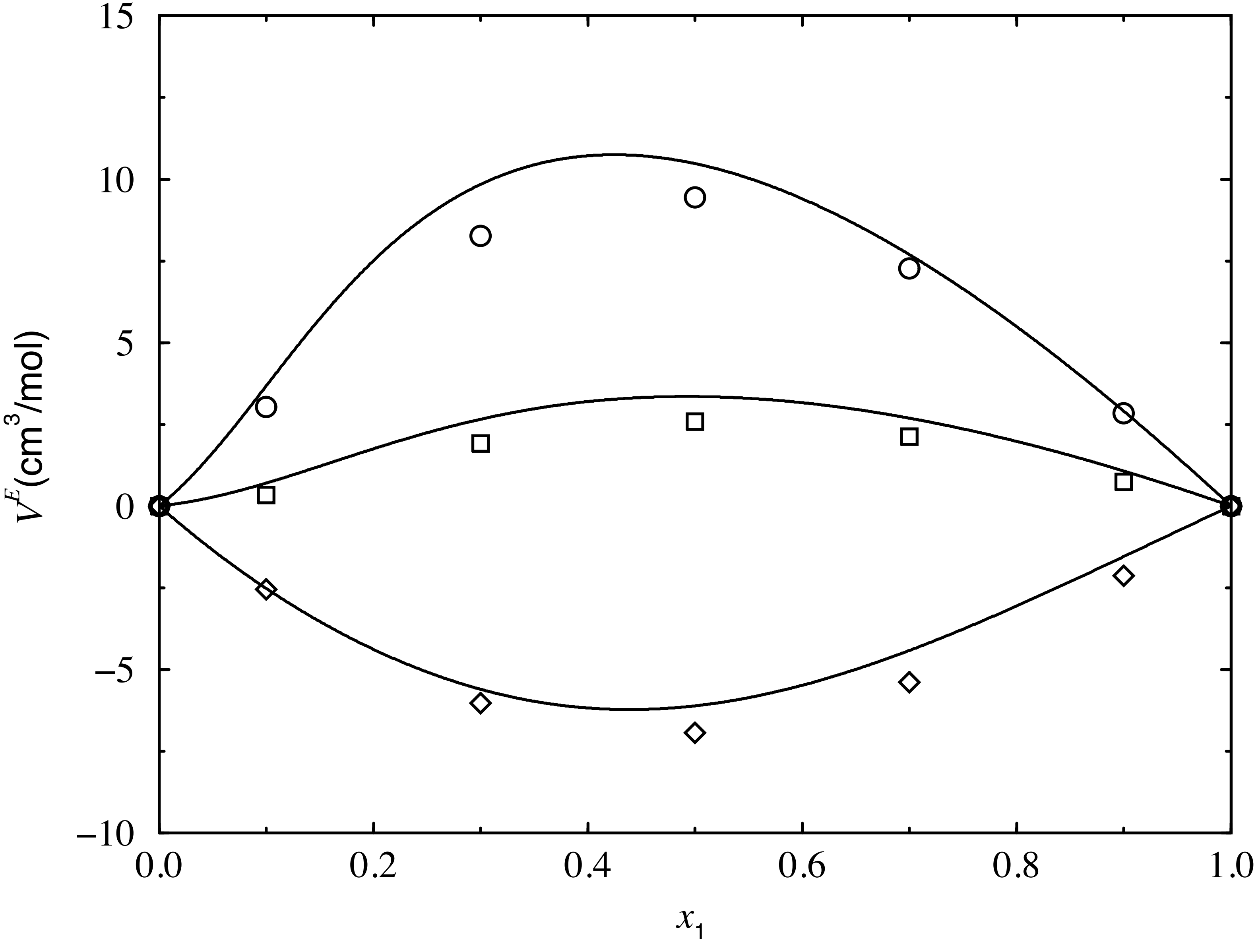

1000
0
−1000
−2000
H^E(J/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1

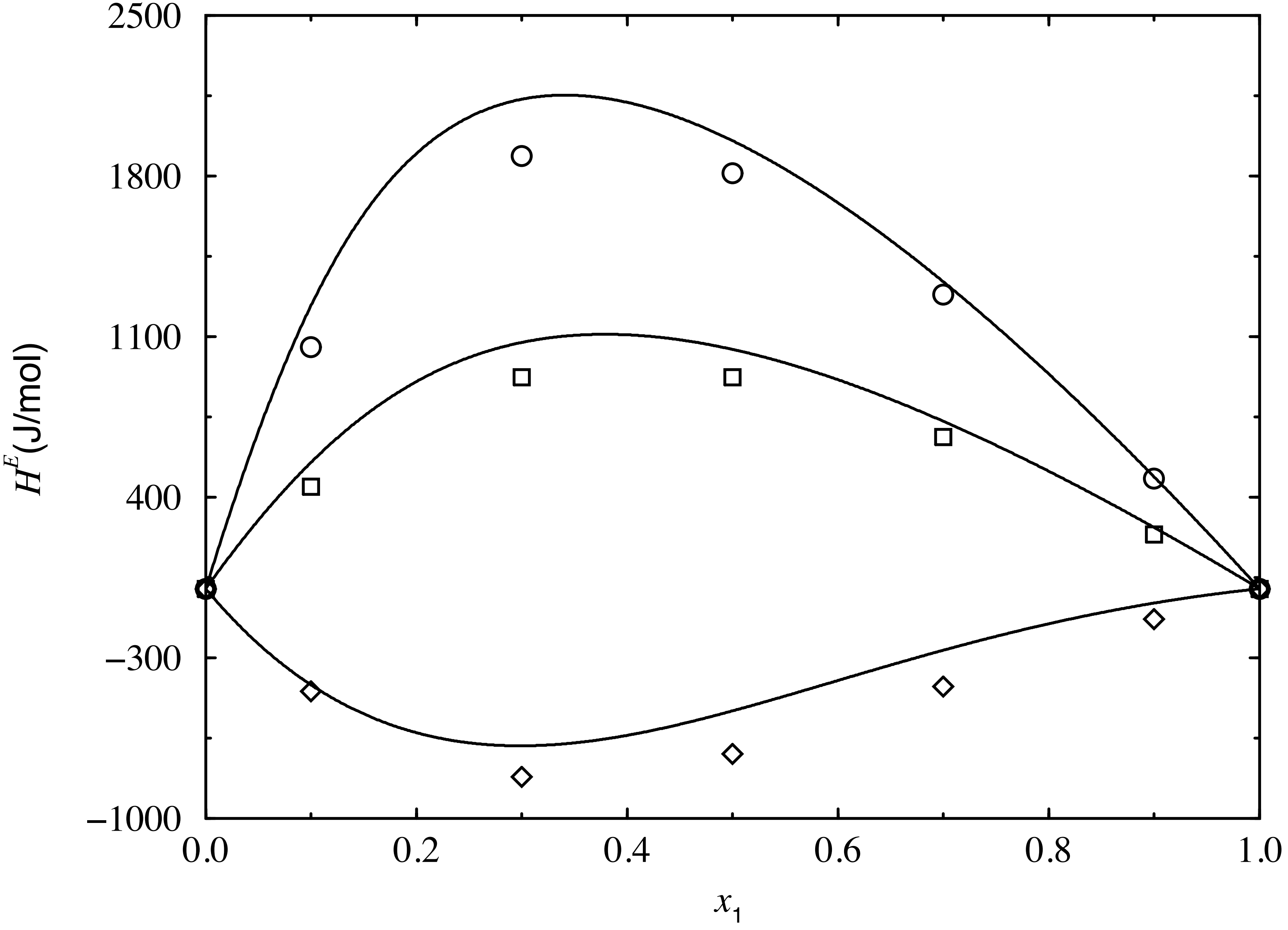

5
0
−5
−10
−15
−20
V^E(cm^3/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1

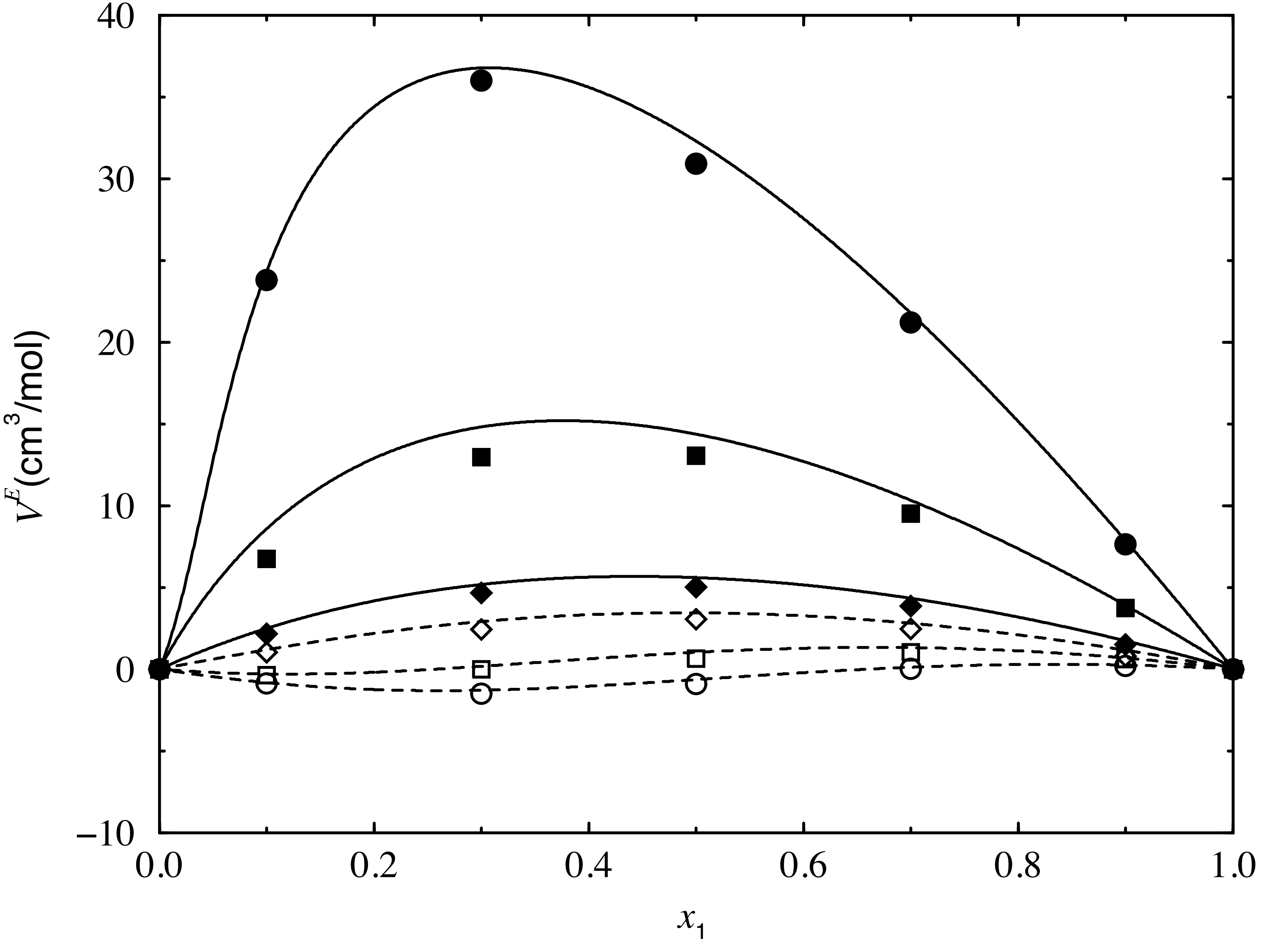

1500
800
100
−600
−1300
−2000
H^E(J/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1


10
6
2
−2
0.0
0.2
0.4
0.6
0.8
1.0
V^E(cm^3/mol)
x_1

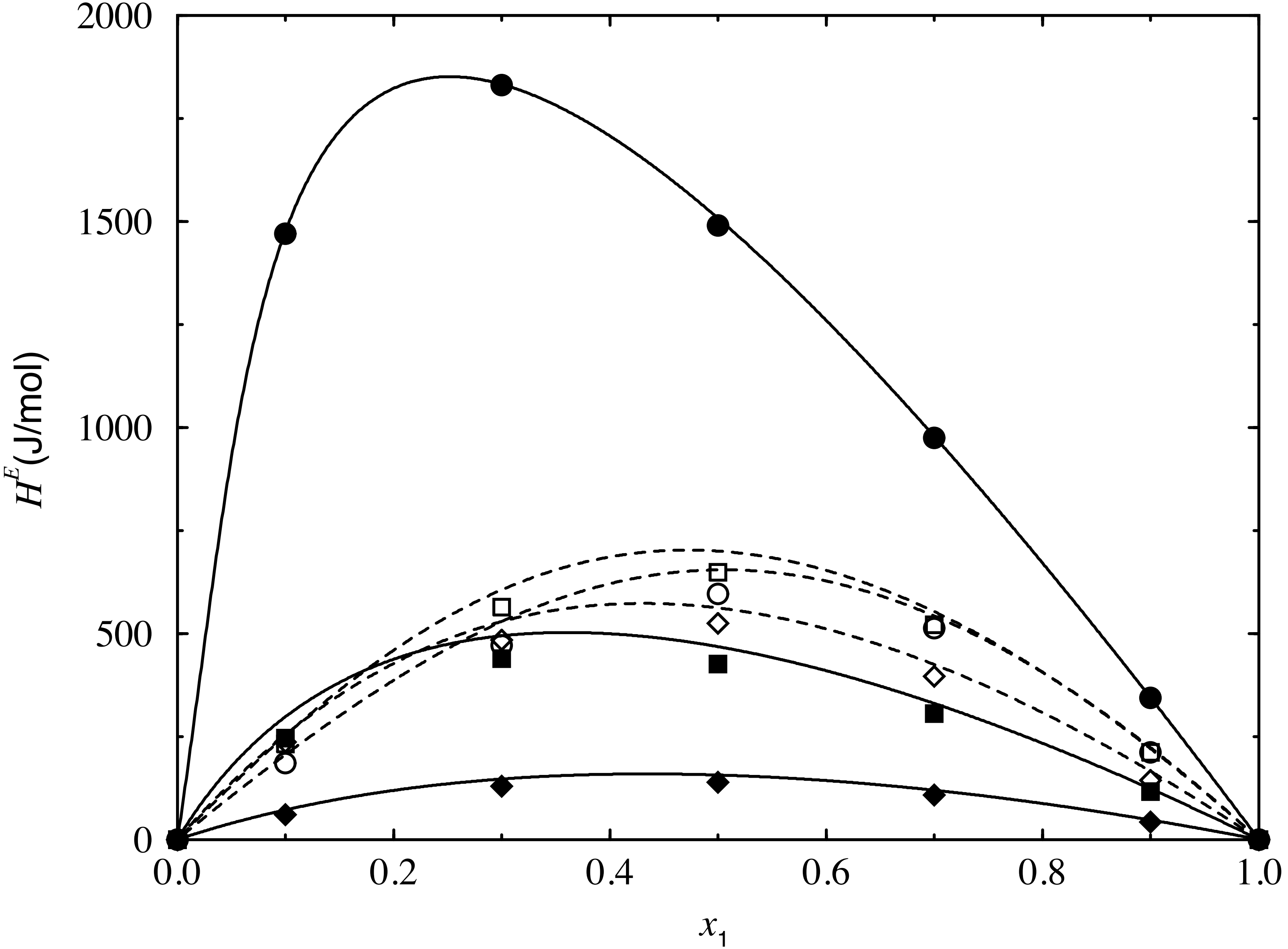

1500
1100
700
300
−100
0.0
0.2
0.4
0.6
0.8
1.0
H^E (J/mol)
x_1

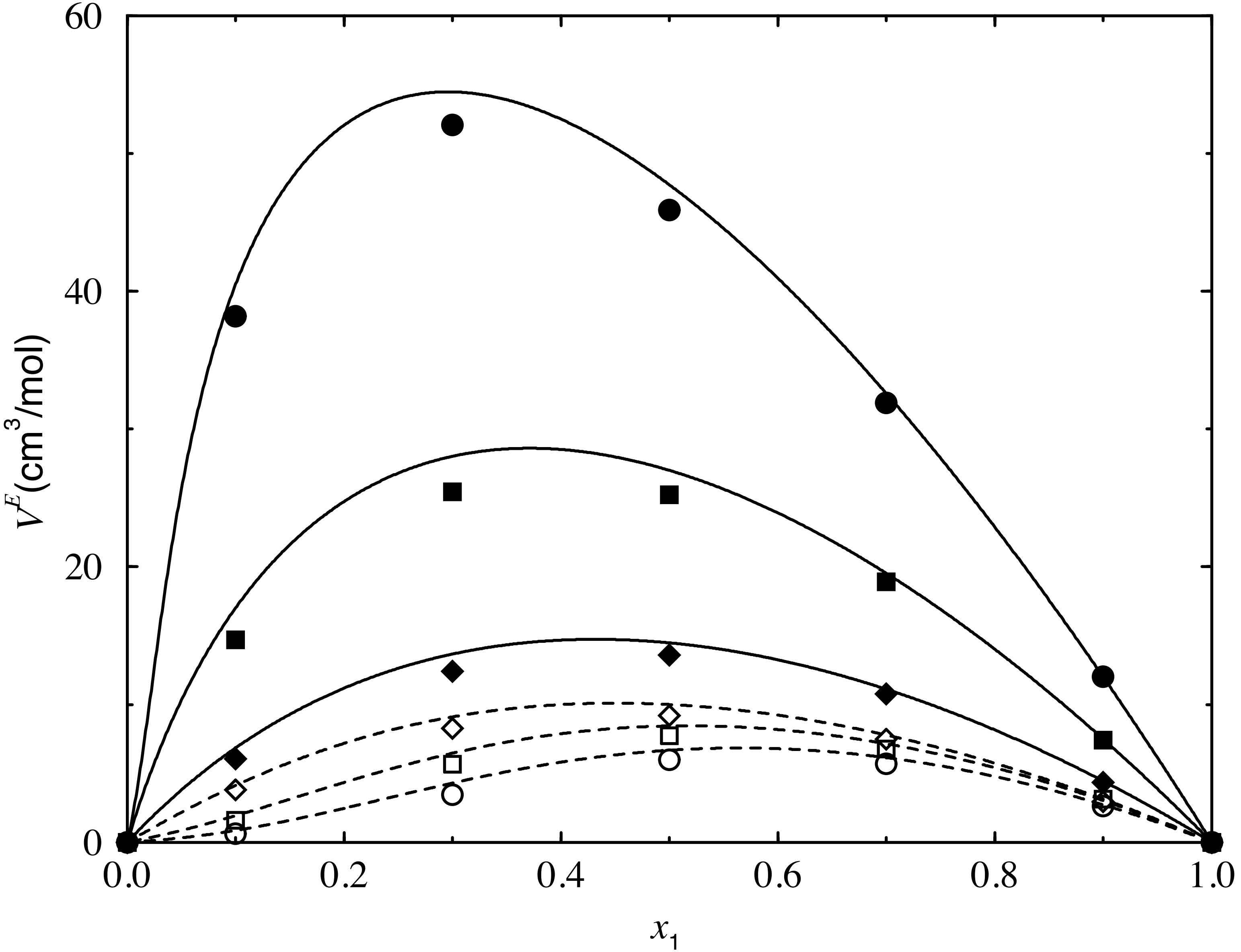

15
10
5
0
−5
−10
V^E(cm^3/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1

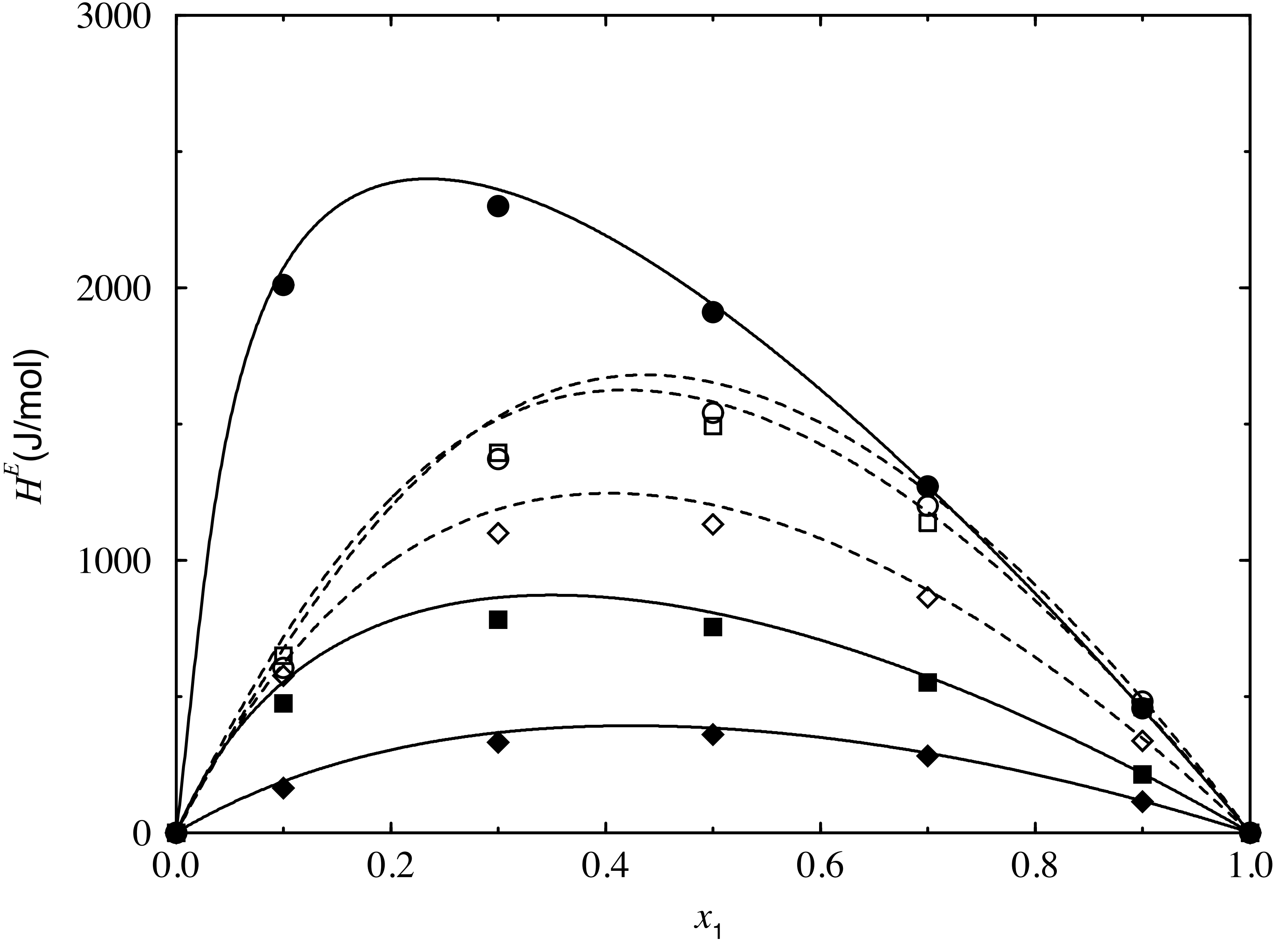

2500
1800
1100
400
−300
−1000
H^E(J/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1

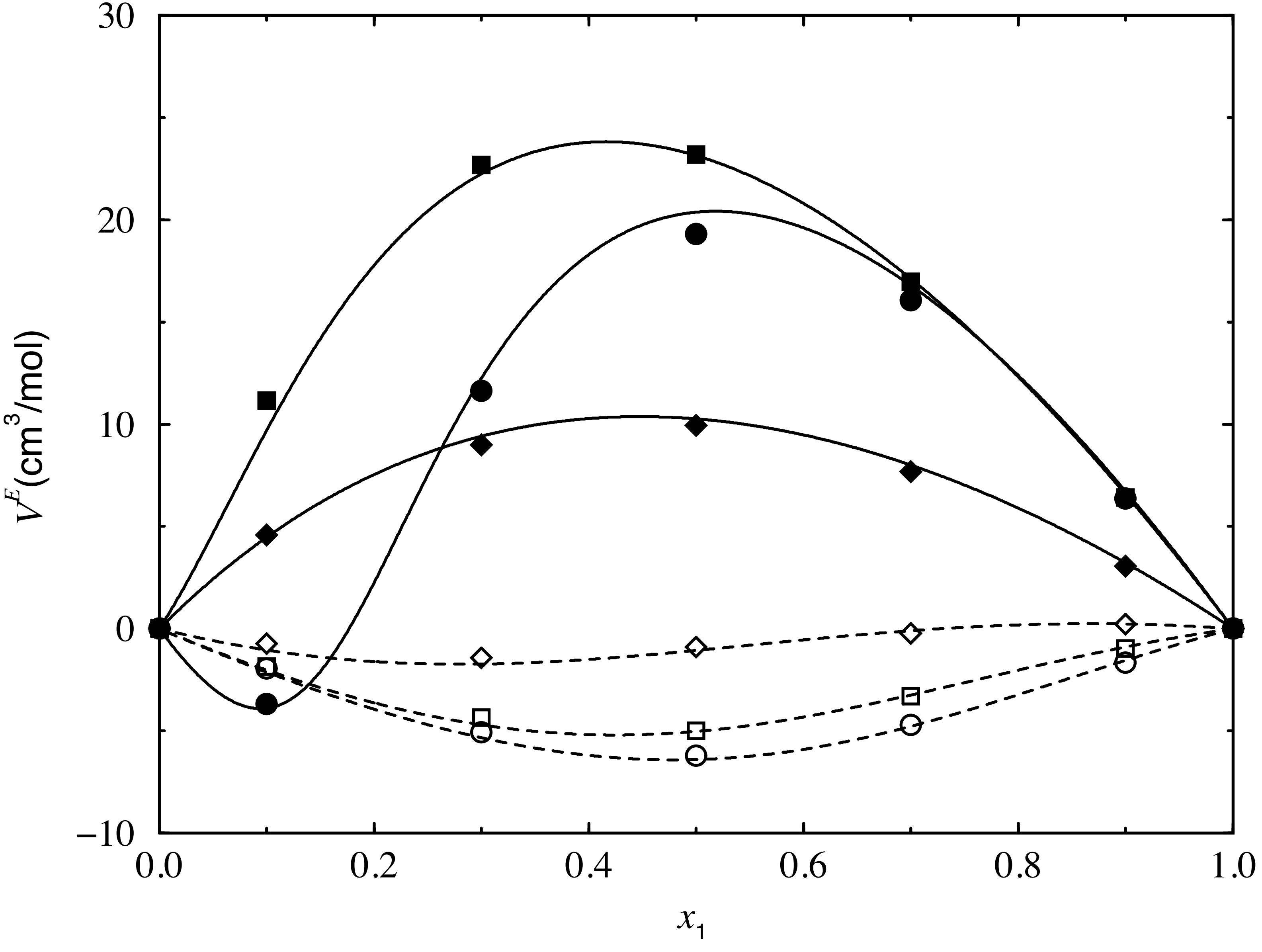


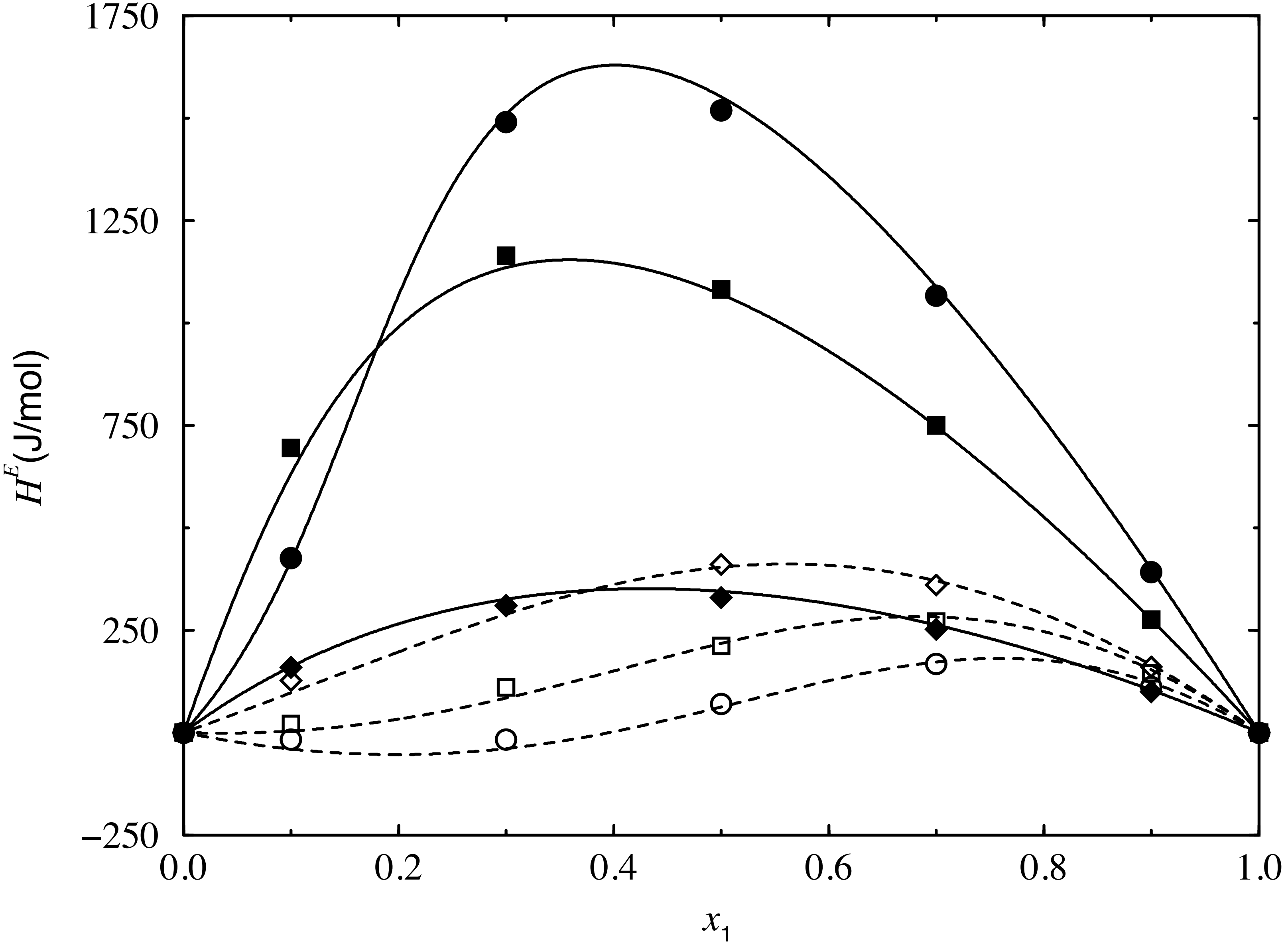
40
30
20
10
0
−10
V^E(cm^3/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1


2000
1500
1000
500
0
H^E(J/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1

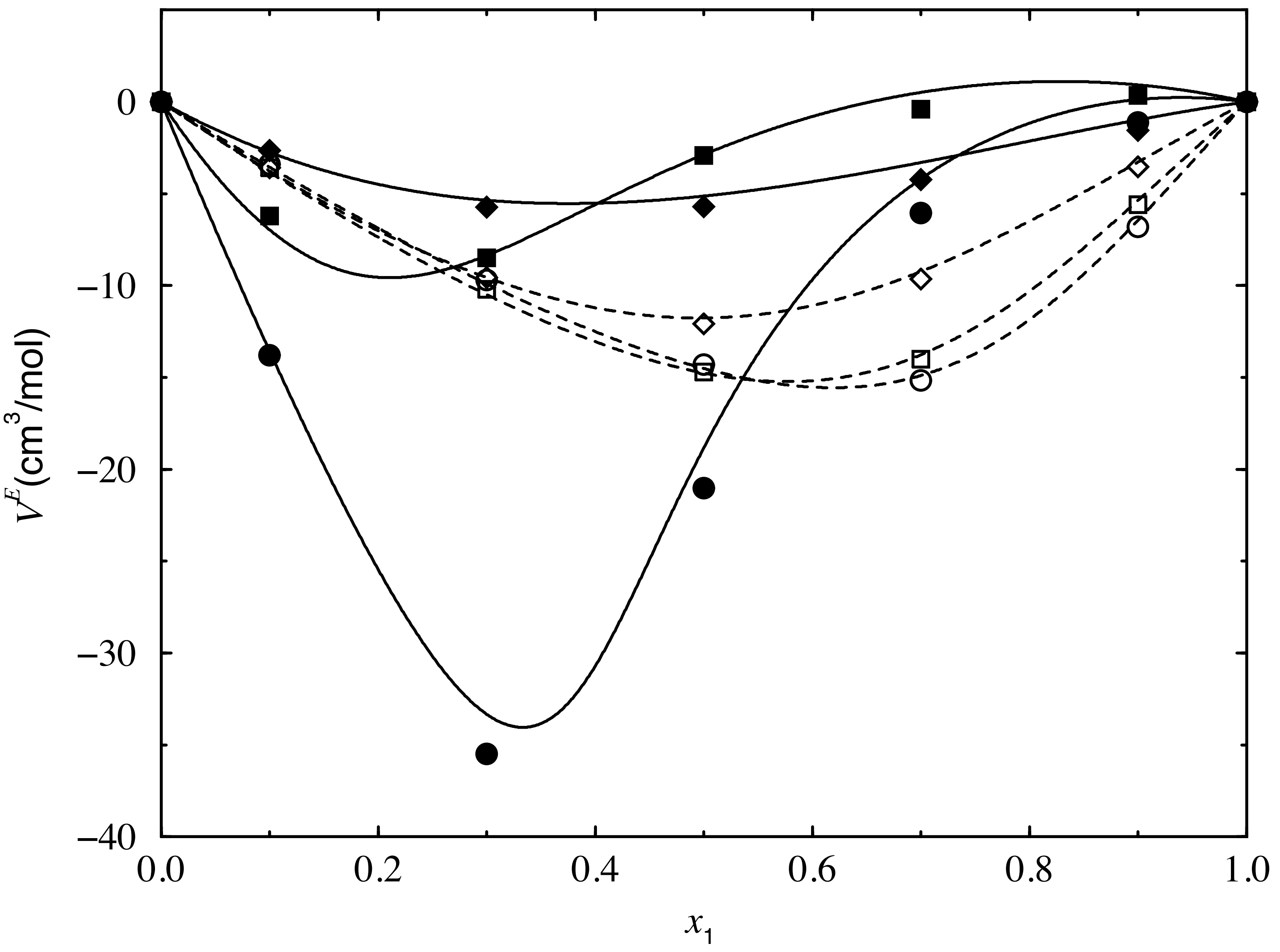

60
40
20
0
V^E(cm^3/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1

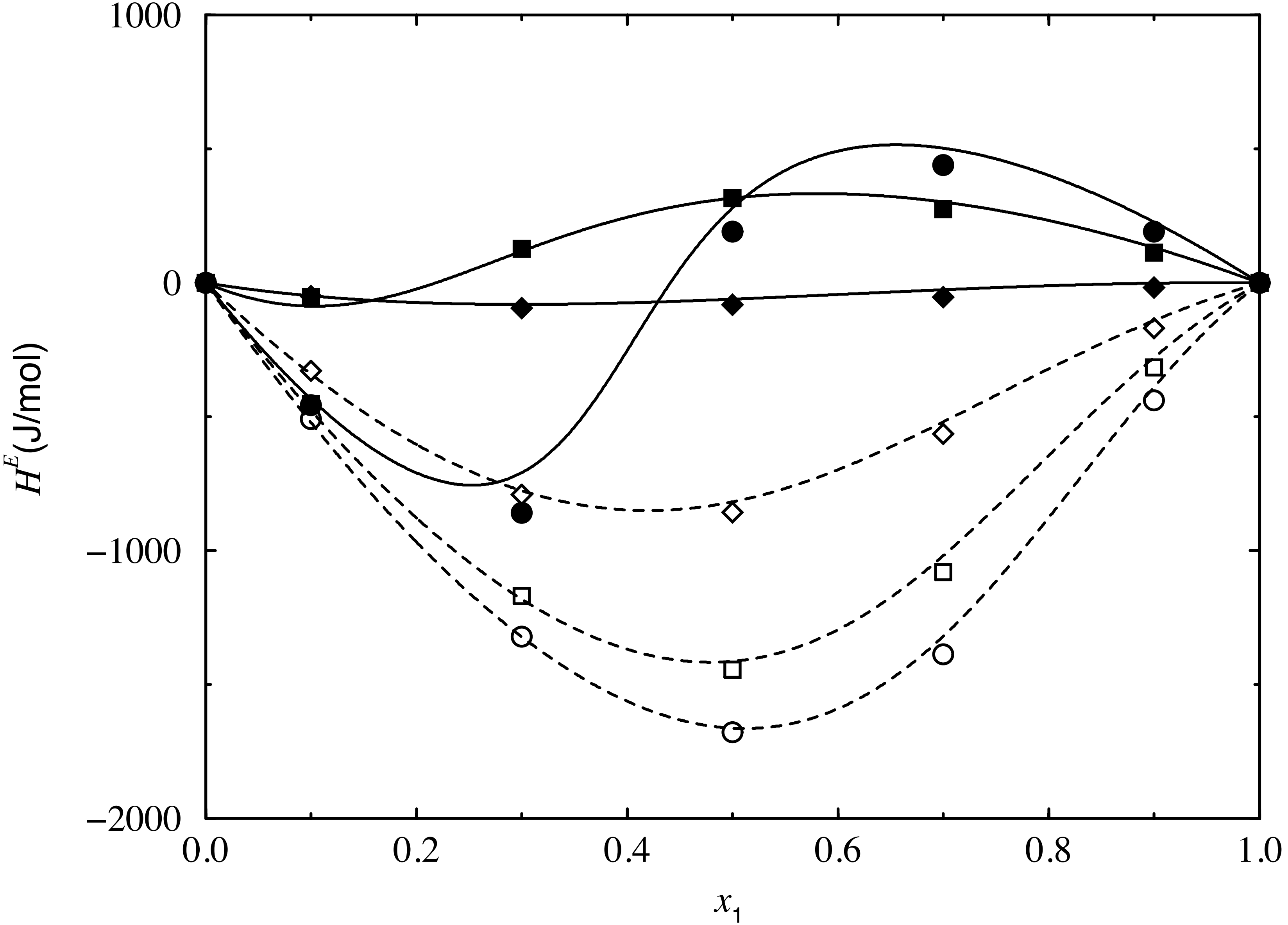

3000
2000
1000
0
H^E(J/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1


30
20
10
0
−10
V^E(cm^3/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1



H^E (J/mol)
1750
1250
750
250
−250
0.0
0.2
0.4
0.6
0.8
1.0
x_1


V^E(cm^3/mol)
0
−10
−20
−30
−40
0.0
0.2
0.4
0.6
0.8
1.0
x_1


1000
0
−1000
−2000
H^E(J/mol)
0.0
0.2
0.4
0.6
0.8
1.0
x_1