ORTJ0952

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Excess enthalpies of trichloromethane + n-alkanes. Measurement and comparison with the DISQUAC model

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Enthalpy-of-mixing measurements are reported at 298.15 K *for trichloromethane + n-alkanes (pentane through heptadecane). All the mixtures are endothermic with molar excess enthalpies increasing regularly with the chain length of the n-alkane. The experimental equimolar values for short-chain n-alkanes agree within better than 4 % with DISQUAC predictions using previously published parameters. Systematic discrepancies (up to 10 %) are noted in mixtures with long-chain n-alkanes.*

1. INTRODUCTION

In continuation of our systematic experimental studies on the excess molar enthalpies H^E of mixtures containing chloroalkanes (**ORTJ0915**), we have determined H^E of trichloromethane + n-alkanes (pentane through heptadecane). These data, along with literature data on vapor-liquid equilibria (see **KEHH0880**) will be used to test the applicability of various group-contribution models. Only a few H^E measurements have been published previously on this class of mixtures.

2. EXPERIMENTAL SECTION

2.1. Apparatus and Procedure

The experimental data were taken at atmospheric pressure by means of a Calvet type microcalorimeter, model MS-80D (SETARAM, Lyon, France) with a stainless steel batch mixing cell (volume ca. 8 cm^3) and with negligible vapor phase. The temperature T was maintained constant to within 0.02 K at (298.15 ± 0.02) K. All temperatures are on ITS-90. The microcalorimeter was calibrated electrically after each measurement (see **ORTJ0881**). Check measurements on cyclohexane + hexane and benzene + heptadecane are in agreement to within 1 % (over central range of concentration) with the data reported in (**MCGM0690**) and (**DIAM0742**). The estimated uncertainties in the mole fraction composition x_i and H^E are, respectively, $\sigma(x_i)$ = 0.0005 and $\sigma(H^E)$ = 0.02 $|H^E|$ (over central range of concentration).

2.2. Materials

$CHCl_3$, Trichloromethane Aldrich Chem. Co., Inc. (Milwaukee, WI, USA) material of stated purity > 99 mole %, was degassed ultrasonically, dried over molecular sieves Type 3A (reference 69828, from Fluka), and used without further purification. n(D,298.15 K) = 1.4429; ρ_i(298.15 K)/kg m^{-3} = 1480.03.

C_5H_{12}, Pentane. Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.5 mole %, purified as above; n(D, 298.15 K) = 1.3547; ρ_i(298.15 K)/kg m^{-3} = 621.31.

C_6H_{14}, Hexane. Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.5 mole %, purified as above; n(D, 298.15 K) = 1.3723; ρ_i(298.15 K)/kg m^{-3} = 654.71.

C_7H_{16}, Heptane. Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.5 mole %, purified as above; n(D, 298.15 K) = 1.3851; ρ_i(298.15 K)/kg m^{-3} = 679.46.

C_8H_{18}, Octane. Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.5 mole %, purified as above; n(D, 298.15 K) = 1.3951; ρ_i(298.15 K)/kg m^{-3} = 698.29.

C_9H_{20}, Nonane. Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 298.15 K) = 1.4033; ρ_i(298.15 K)/kg m^{-3} = 713.85.

$C_{10}H_{22}$, Decane. Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 298.15 K) = 1.4098; ρ_i(298.15 K)/kg m^{-3} = 726.13.

$C_{11}H_{24}$, Undecane. Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 98.0 mole %, purified as above; n(D, 298.15 K) = 1.4154; ρ_i(298.15 K)/kg m^{-3} = 736.80.

$C_{12}H_{26}$, Dodecane. Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 98.0 mole %, purified as above; n(D, 298.15 K) = 1.4196; ρ_i(298.15 K)/kg m^{-3} = 745.19.

$C_{13}H_{28}$, Tridecane. Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.5 mole %, purified as above; n(D, 298.15 K) = 1.4238; ρ_i(298.15 K)/kg m^{-3} = 752.79.

$C_{14}H_{30}$, Tetradecane. Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.5 mole %, purified as above; n(D, 298.15 K) = 1.4271; ρ_i(298.15 K)/kg m^{-3} = 759.36.

$C_{15}H_{32}$, Pentadecane. Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 98 mole %, purified as above; n(D, 298.15 K) = 1.4298; ρ_i(298.15 K)/kg m^{-3} = 764.80.

$C_{16}H_{34}$, Hexadecane. Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 98 mole %, purified as above; n(D, 298.15 K) = 1.4325; ρ_i(298.15 K)/kg m^{-3} = 770.10.

$C_{17}H_{36}$, Heptadecane. Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 99 mole %, purified as above; n(D, 298.15 K) = 1.4347; ρ_i(298.15 K)/kg m^{-3} = 774.33.

3. RESULTS

The direct experimental H^E values are tabulated and graphed in the Appendix and saved on disk as Standard ELDATA Files **ORTJ0952.001** through **ORTJ0952.013.**

The data were fitted to Eq. (1):

$$H^E_{calc}/\text{J mol}^{-1} = x_1x_2\Sigma A_i[x_1/(x_1 + kx_2)]^{i-1} \qquad (1)$$

all points weighted equally. With an adjusted coefficient k and n = 4 coefficients A_i the standard deviations $\sigma(H^E)$, defined by Eq.(2):

$$\sigma(H^E) = [\Sigma(H^E_{calc} - H^E)^2/(N-n)]^{1/2} \qquad (2)$$

where N is the number of experimental values, are less than 10 J mol^{-1} (ca. 0.4 % at x_1 = 0.5).

4. DISCUSSION AND CONCLUSIONS

Reliable H^E data at 298.15 K exist in the literature for $CHCl_3$ + n-hexane (**BIST0710**), + n-heptane (**BIST0710, ABEL0730, BIRJ0780**), and + n-hexadecane (**ABEL0730, BIRJ0780**) and are in good agreement (2.5 % for n-hexane and less than 1 % for the remaining n-alkanes, at x_1 = 0.5). All the mixtures are endothermic with H^E increasing regularly with the chain length of the n-alkane. The experimental equimolar H^E values for short-chain n-alkanes agree within better than 4 % with DISQUAC predictions, using previously published parameters (**KEHH0880**). Characteristic discrepancies (up to 10 %) are noted in mixtures with long-chain n-alkanes. These are usually attributed to the perturbation of the conformational order of long-chain n-alkanes when mixed with globular molecules such as $CHCl_3$ (**PATD0760**).

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Ortega, Juan* [ORTJ0]
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Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION **ORTJ0952.001**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. C_5H_{12}, Pentane

[P1] = .298150E+03

[X1]	[Y1]
.790000E−01	.137500E+03
.158700E+00	.285400E+03
.241000E+00	.430100E+03
.317600E+00	.545900E+03
.386700E+00	.623800E+03
.450800E+00	.670700E+03
.508200E+00	.692100E+03
.560300E+00	.695600E+03
.604500E+00	.680400E+03
.643600E+00	.657500E+03
.674900E+00	.630100E+03
.723900E+00	.574600E+03
.772600E+00	.504800E+03
.823100E+00	.424500E+03
.871400E+00	.319100E+03
.918800E+00	.205800E+03
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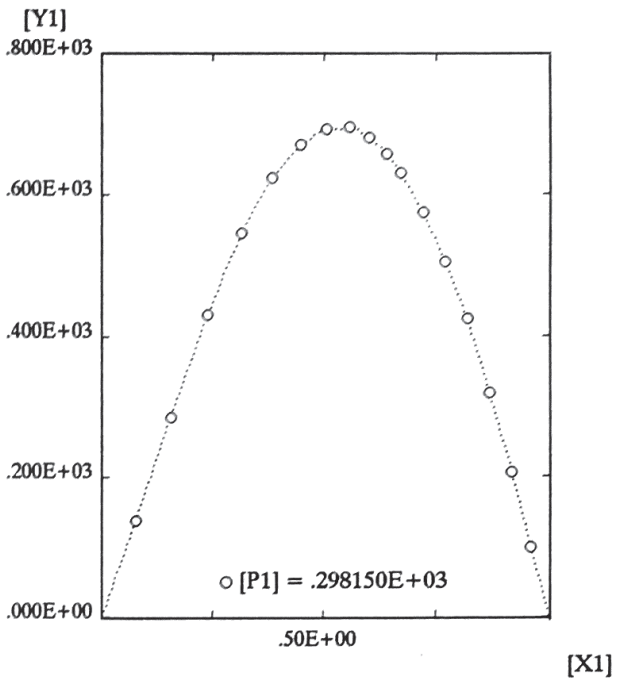

Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION **ORTJ0952.002**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. C_6H_{14}, Hexane

[P1] = .298150E+03

[X1]	[Y1]
.809000E−01	.153100E+03
.168700E+00	.355200E+03
.253300E+00	.473900E+03
.334300E+00	.605800E+03
.407100E+00	.687300E+03
.471400E+00	.726600E+03
.533400E+00	.746100E+03
.582600E+00	.739700E+03
.625300E+00	.722600E+03
.662300E+00	.697800E+03
.706600E+00	.657300E+03
.752600E+00	.602200E+03
.799600E+00	.527400E+03
.840600E+00	.440300E+03
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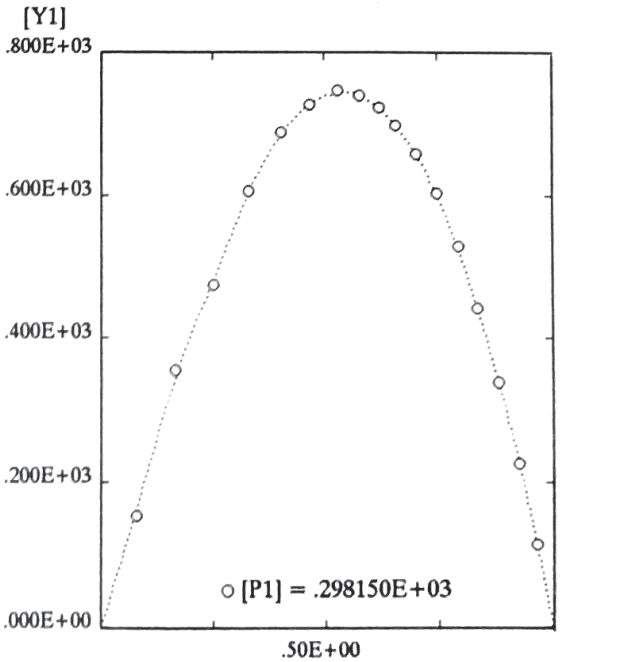
.967400E+00	.113400E+03



Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION **ORTJ0952.003**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. C_7H_{16}, Heptane

[P1] = .298150E+03

[X1]	[Y1]
.931000E−01	.208200E+03
.187000E+00	.403400E+03
.277100E+00	.568200E+03
.358400E+00	.681600E+03
.433800E+00	.760800E+03
.498700E+00	.798900E+03
.555900E+00	.806700E+03
.604300E+00	.793200E+03
.647200E+00	.767300E+03
.683000E+00	.730400E+03
.694800E+00	.714600E+03
.736200E+00	.661400E+03
.778400E+00	.592100E+03
.820800E+00	.517900E+03
.863100E+00	.428400E+03
.899700E+00	.327600E+03
.938100E+00	.217000E+03
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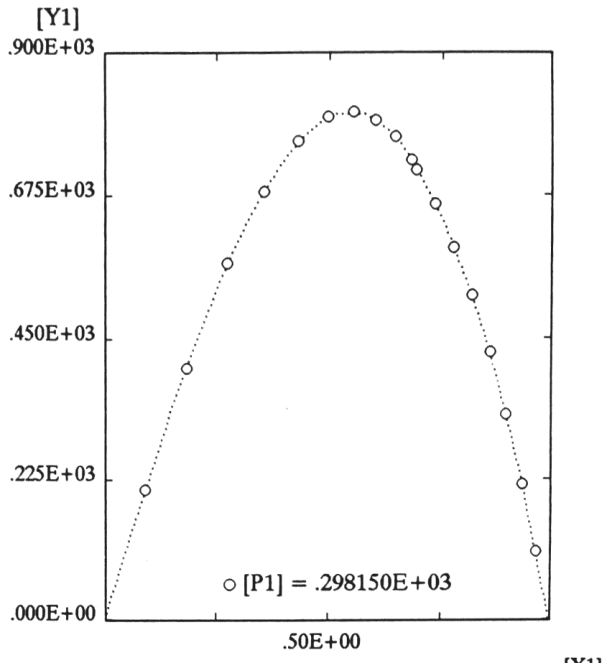

Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION **ORTJ0952.004**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. C_8H_{18}, Octane

[P1] = .298150E+03

[X1]	[Y1]
.996000E−01	.235000E+03
.198000E+00	.450800E+03
.293700E+00	.629000E+03
.379000E+00	.757800E+03
.453300E+00	.830200E+03
.519300E+00	.866000E+03
.576000E+00	.870100E+03
.624900E+00	.854700E+03
.666800E+00	.811900E+03
.701600E+00	.760900E+03
.737800E+00	.699100E+03
.782100E+00	.625400E+03
.827800E+00	.528800E+03
.871900E+00	.422900E+03
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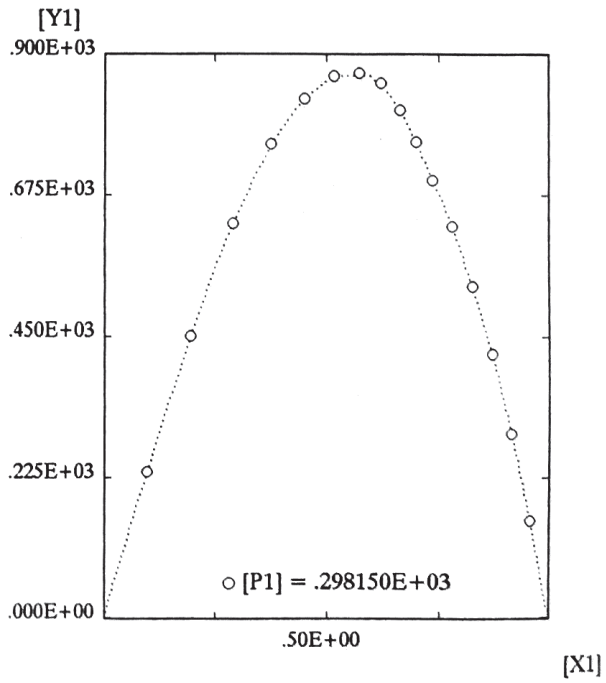

ORTJ0952.005

Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. C_9H_{20}, Nonane

[P1] = .298150E+03

[X1]	[Y1]
.125200E+00	.315500E+03
.236700E+00	.540900E+03
.338900E+00	.730900E+03
.427900E+00	.857300E+03
.502800E+00	.909300E+03
.567600E+00	.922600E+03
.622200E+00	.903500E+03
.663000E+00	.862600E+03
.697700E+00	.821500E+03
.735300E+00	.765900E+03
.775900E+00	.685300E+03
.814800E+00	.606500E+03
.852800E+00	.512400E+03
.885700E+00	.418400E+03
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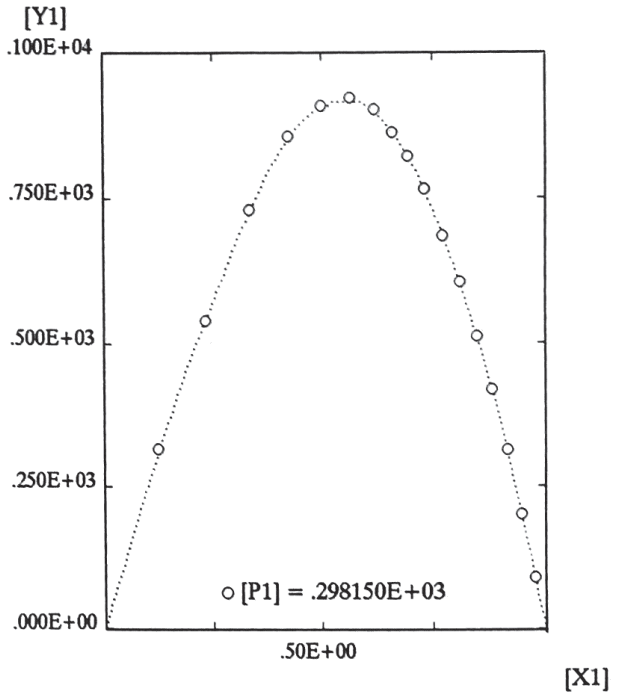

ORTJ0952.006

Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. $C_{10}H_{22}$, Decane

[P1] = .298150E+03

[X1]	[Y1]
.101200E+00	.275900E+03
.192700E+00	.485400E+03
.272700E+00	.649900E+03
.346300E+00	.779200E+03
.405400E+00	.860600E+03
.461500E+00	.916500E+03
.512400E+00	.949300E+03
.557300E+00	.962300E+03
.595800E+00	.957700E+03
.666700E+00	.894600E+03
.703100E+00	.850700E+03
.738400E+00	.802000E+03
.777600E+00	.724700E+03
.817700E+00	.640700E+03
.857300E+00	.538500E+03
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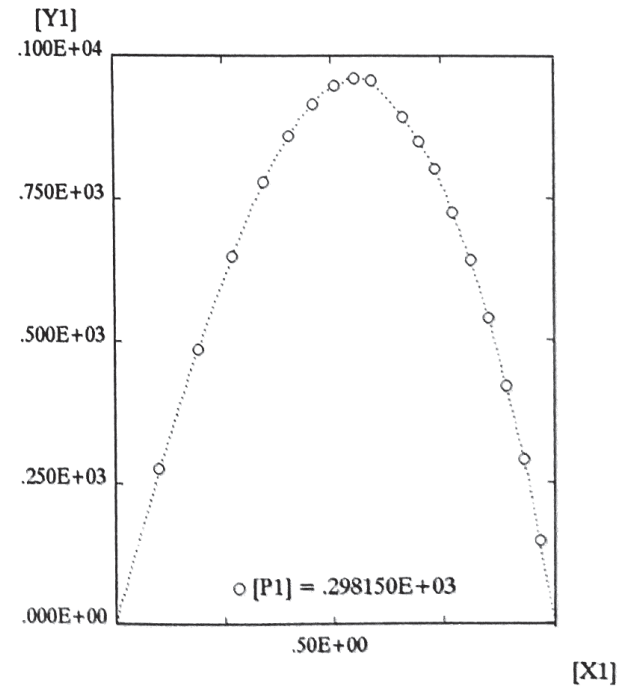

ORTJ0952.007

Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. $C_{11}H_{24}$, Undecane

[P1] = .298150E+03

[X1]	[Y1]
.131200E+00	.339400E+03
.253000E+00	.591900E+03
.358900E+00	.801100E+03
.447900E+00	.927800E+03
.524100E+00	.990800E+03
.580800E+00	.100240E+04
.628000E+00	.988600E+03
.667100E+00	.959100E+03
.698500E+00	.920900E+03
.756800E+00	.821500E+03
.796000E+00	.732800E+03
.834400E+00	.629600E+03
.874700E+00	.519000E+03
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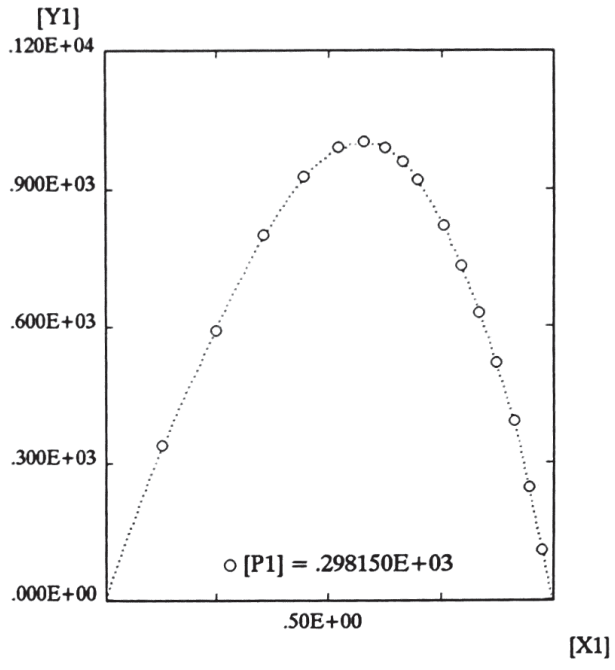

ORTJ0952.008

Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. $C_{12}H_{26}$, Dodecane

[P1] = .298150E+03

[X1]	[Y1]
.972000E−01	.265700E+03
.192900E+00	.484600E+03
.278100E+00	.673500E+03
.352500E+00	.812900E+03
.418800E+00	.912900E+03
.475000E+00	.975800E+03
.525800E+00	.101380E+04
.569400E+00	.102760E+04
.608800E+00	.102490E+04
.643400E+00	.100940E+04
.682700E+00	.970300E+03
.715900E+00	.925800E+03
.730200E+00	.902900E+03
.765600E+00	.830500E+03
.802000E+00	.750200E+03
.837700E+00	.659700E+03
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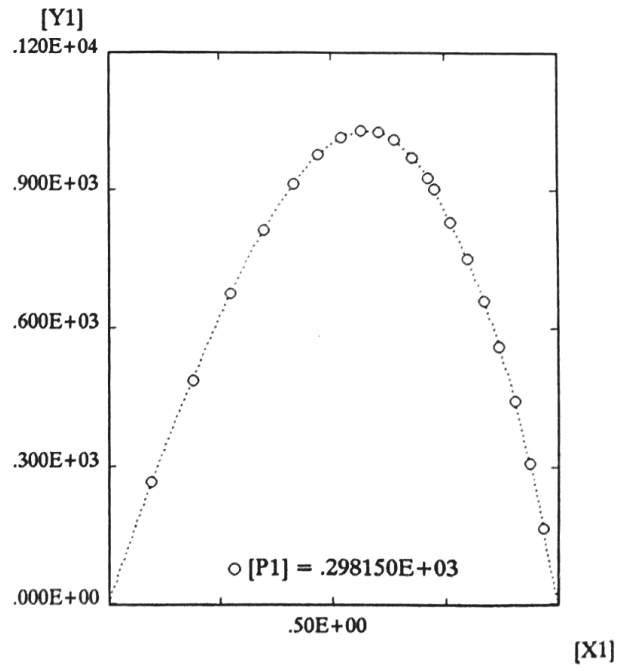

Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION **ORTJ0952.009**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. $C_{13}H_{28}$, Tridecane

[P1] = .298150E+03

[X1]	[Y1]
.124100E+00	.363200E+03
.230800E+00	.605200E+03
.318100E+00	.775900E+03
.396600E+00	.911300E+03
.462400E+00	.995000E+03
.519800E+00	.103980E+04
.566700E+00	.105620E+04
.608900E+00	.105610E+04
.645900E+00	.104240E+04
.688900E+00	.994700E+03
.725200E+00	.950700E+03
.750700E+00	.895800E+03
.786200E+00	.826300E+03
.821900E+00	.732400E+03
.854600E+00	.642800E+03
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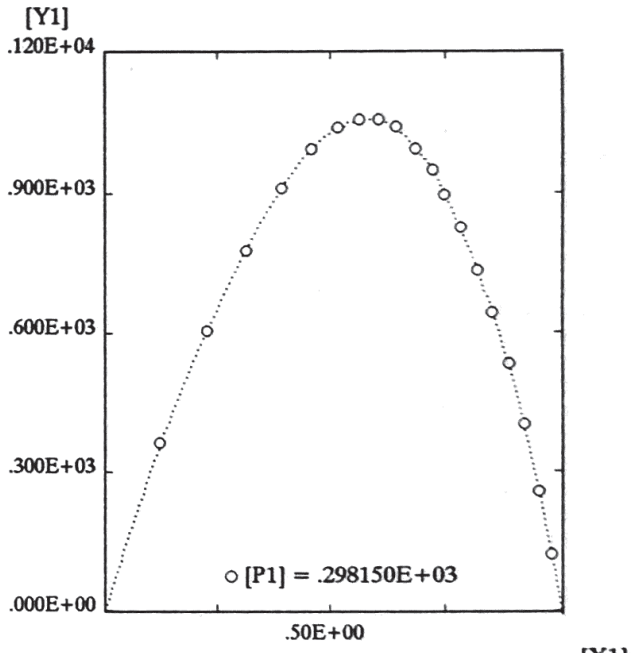
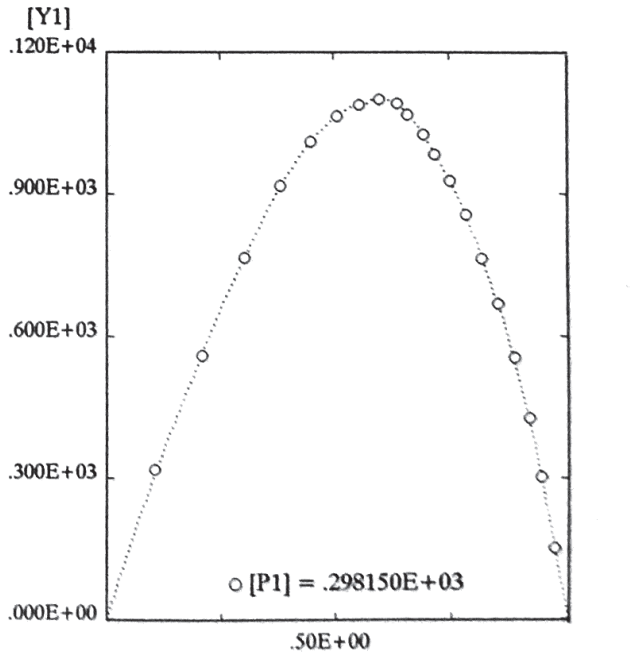


Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION **ORTJ0952.010**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. $C_{14}H_{30}$, Tetradecane

[P1] = .298150E+03

[X1]	[Y1]
.106900E+00	.318100E+03
.211400E+00	.559700E+03
.305300E+00	.766100E+03
.384600E+00	.917400E+03
.451900E+00	.101010E+04
.510900E+00	.106380E+04
.558000E+00	.108880E+04
.602300E+00	.110040E+04
.641400E+00	.109160E+04
.663100E+00	.106710E+04
.697200E+00	.102530E+04
.720700E+00	.983700E+03
.753700E+00	.927000E+03
.787700E+00	.855200E+03
.821600E+00	.762100E+03
.855900E+00	.667500E+03
.889500E+00	.556000E+03
.921600E+00	.428400E+03
.946000E+00	.301800E+03
.974700E+00	.150100E+03

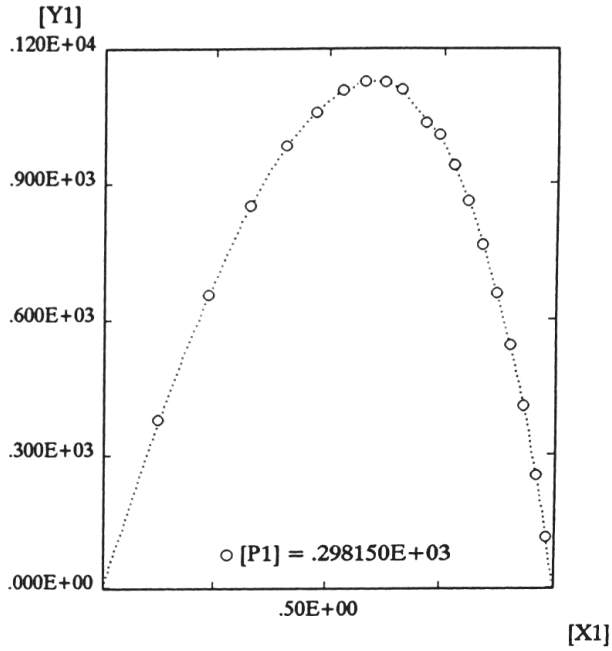


Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION **ORTJ0952.011**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. $C_{15}H_{32}$, Pentadecane

[P1] = .298150E+03

[X1]	[Y1]
.125000E+00	.379100E+03
.237700E+00	.656800E+03
.330600E+00	.851000E+03
.408200E+00	.984600E+03
.475000E+00	.105950E+04
.532200E+00	.110870E+04
.580800E+00	.112800E+04
.624300E+00	.112790E+04
.660000E+00	.111080E+04
.712900E+00	.103550E+04
.742800E+00	.100800E+04
.775400E+00	.939100E+03
.806700E+00	.860000E+03
.839400E+00	.764900E+03
.872400E+00	.658300E+03
.904300E+00	.542200E+03
.933500E+00	.407700E+03
.963200E+00	.253900E+03
.986300E+00	.114900E+03

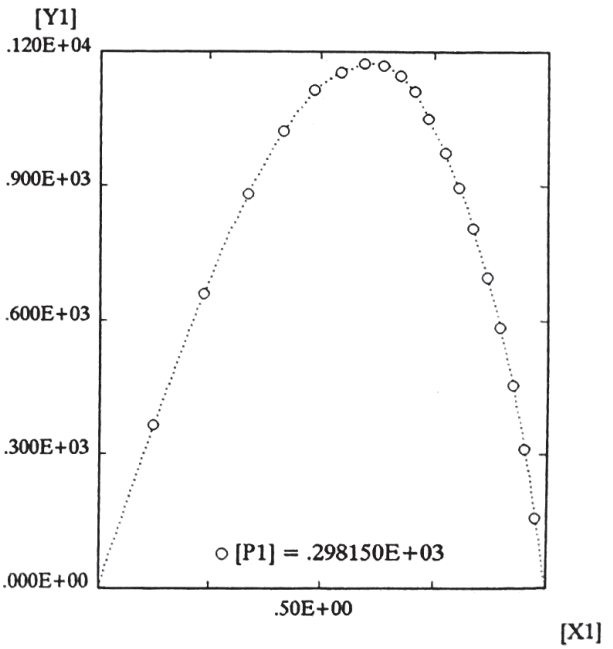


Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION **ORTJ0952.012**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy
Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components: **1. CHCl3, Trichloromethane**
2. $C_{16}H_{34}$, Hexadecane

[P1] = .298150E+03

[X1]	[Y1]
.125200E+00	.364000E+03
.239800E+00	.659900E+03
.339400E+00	.881500E+03
.418900E+00	.102180E+04
.489000E+00	.111520E+04
.548100E+00	.115370E+04
.598600E+00	.117390E+04
.641600E+00	.116880E+04
.678800E+00	.114720E+04
.710100E+00	.111220E+04
.740300E+00	.105140E+04
.776600E+00	.974500E+03
.807600E+00	.896500E+03
.839000E+00	.805400E+03
.869800E+00	.696200E+03
.898000E+00	.585200E+03
.927100E+00	.455500E+03
.953300E+00	.311400E+03
.979000E+00	.156000E+03



Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION

ORTJ0952.013

State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid

Parameters:
Variables:
[P1] T/K, Temperature
[X1] x_1/-, Mole fraction of component 1
[Y1] H^E/Jmol^{-1}, Molar excess enthalpy

Method: Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant T

Components:
1. **CHCl3, Trichloromethane**
2. **$C_{17}H_{36}$, Heptadecane**

[P1] = .298150E+03

[X1]	[Y1]
.155200E+00	.472200E+03
.272000E+00	.775800E+03
.369700E+00	.991100E+03
.447800E+00	.112030E+04
.508500E+00	.117950E+04
.556600E+00	.121350E+04
.598600E+00	.124630E+04
.637500E+00	.124180E+04
.666400E+00	.121820E+04
.689700E+00	.118170E+04
.733200E+00	.112160E+04
.764200E+00	.105420E+04
.795800E+00	.981300E+03
.827700E+00	.880900E+03
.859200E+00	.768500E+03
.890600E+00	.645200E+03
.920700E+00	.509700E+03
.950300E+00	.349900E+03
.978200E+00	.172900E+03