On Thermodynamic Characteristics of In–I System Compounds

V. A. Titov*, T. P. Chusova, and Yu. G. Stenin

Novosibirsk (Russia), Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences

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Abstract. The temperature dependences of the total vapour pressure for solid and liquid InI_2 and liquid InI_3 were measured by the static method with a membran-gauge manometer. The heat capacities above phases and solid InI_3 were also obtained. The partial pressures In_2I_6, InI_3, InI, In_2I_4, I_2, I were calculated. Absolute entropies and enthalpies of formation InI_2 (crII), InI_2 (l), In_2I_4 (g), InI_3 (l), InI_3 (g), In_2I_6 (g) were obtained. We used the least square method to obtain the mutual consistent sets of data on thermodynamic characteristics of indium iodides in condensed and gaseous phases. The result of this work is the set of standard formation enthalpies and absolute entropies of the In–I system compounds.

Keywords: Indium iodides; Thermodynamic data

Thermodynamische Daten von Indiumiodid

Inhaltsübersicht. Die Messungen des Gesamtdruckes über InI_3 (fl), InI_2 (f) und InI_2 (fl) werden mit der statischen Methode mit einem Quarz-Membran-Manometer ausgeführt. Die Temperaturabhängigkeiten der spezifischen Wärmen werden für festes und flüssiges InI_2 und InI_3 bestimmt. Die Partialdrücke für In_2I_6, InI_3, InI, In_2I_4, I_2, I werden berechnet. Daraus werden die Bildungenthalpien und Standardentropien von InI_2 (crII), InI_2 (fl), In_2I_4 (g), InI_3 (fl), InI_3 (g), In_2I_6 (g) abgeleitet. Abschließend wird ein kompletter Satz von thermodynamischen Daten für das System Indium–Iod vorgeschlagen.

Introduction

The measurement of the vapour total pressure as a function of temperature and vapour density in a wide concentration range permits us to design various thermodynamic cycles. Such an approach allows one to determine the thermodynamic characteristics of examined compounds in the investigated system, to avoid possible systematic errors and to get the mutual consistent thermodynamic data table. Such an investigation and its advantages have been demonstrated by the author of [1] for the Ge–I system. We have tried to apply a similar approach for study of the properties of the In–I system compounds.

According to the literature data three individual compounds InI, InI_2 and InI_3 in the In–I system are known to exist in crystalline state. Polymorphic transitions for indium diiodide and indium triiodide have been determined reliably. However, different information on temperatures of these transitions has been presented in literature [2–6]: from 426 to 435 K for InI_2 and from 200 to 342 K for InI_3. According to [7–8], In_2I_6, InI_3, InI_2, InI, and I_2 are the main species in the gas phase. But, electronographic vapour investigations performed in the In–I system [9] has some doubt whether the amount of InI_2 being considerable or not. Besides, the presence of In_2I_4 dimers is revealed. The latter conclusion is indirectly confirmed by the data of [6] on the structure of solid indium diiodide.

Experimental

Indium iodides were synthesized from the elements in sealed quartz ampoules under vacuum. Indium, grade HP 50-4 (High Pure 50-4) (impurities sum of 50 controlled elements is not more than 10^{-4} at.%), and iodine, grade HP 16-4 (impurities sum of 16 controlled elements is not more than 10^{-4} at.%) were used. Iodine was resublimated three times in vacuum for additional purification from other halogens and organic impurities; its vapour being overheated up to 1300 K. Monoiodide was synthesized in the excess of indium and triiodide – in excess of iodine. The synthesis was performed in a three section ampoule, initial reagents were loaded into the side sections. Iodine temperature was held at 400 K. The indium temperature was chosen in such a way, that the reaction product pressure did not exceed the iodine pressure. The synthesis being over the product was purified in the same ampoule by its distillation into the central section. The impurities being more volatile and the iodine excess were collected in the section previously occupied by iodine. For this purpose the section was cooled by liquid nitrogen. Indium diiodide was synthesized via melting stoichiometric amounts of InI and InI_3. The purification was performed by freezing out light volatile impurities in liquid nitrogen. The InI_3 synthesis from elements yields the *high temperature*

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* Prof. Dr. V. A. Titov
Institute of Inorganic Chemistry
Russian Academy of Sciences, Sibirian Branch
3 Lavrentiev av.
Novosibirsk 90/Russia

Table 1 Chemical analyses of samples

	Sample No	Obtained, mass%		Calculated, mass.%	
		In	I	In	I
InI	N 3	47.57 ± 0.11	52.49 ± 0.17	47.50	52.50
InI_2	N 5	31.06 ± 0.15	68.79 ± 0.16	31.15	68.85
InI_3	N 1	23.14 ± 0.18	76.67 ± 0.16	23.17	76.83

phase – “yellow” triiodide one (**InI_3(cr. I)**). Its transition to the *low temperature “red” phase (*(**InI_3 (cr. II)**) is kinetically restricted. The “red” phase was prepared via the “yellow” phase recrystallization from its solution in purified n-butyliodide according to the procedure described elsewhere [10]. All the compounds obtained were characterized by chemical, spectral and X-ray powder diffraction analysis. The indium content was controlled by the weight method (In_2O_3). The iodine content was measured by potentiometric titration using $AgNO_3$. The results of three typical samples (three parallel runs were carried for every sample) are presented in Table 1, errors being given for 95% reliable intervales. Spectral analysis showed the sum of all impurities controlled to be not more than 0.015 at.%. According to the X-ray power diffraction results all the samples were found to be single phases. Unfortunately, in the reference books there are no X-ray power diffraction data for InI_2 and InI_3. Hence, we have recorded their Raman scattering spectra which agree well with previously obtained data [6, 11]. All the operations with the samples were carried out in such a way that contact with moisture and atmosphere gases was excluded.

Experimental Device and Measurements

To determine the heat capacities of condensed phases we have used the drop calorimetry allowing us to measure $H^0(T)–H^0(298)$ ($P^0 = 101{,}325$ kPa) temperature dependence [12]. The experiments were performed on samples placed into 25–30 mm long quartz ampoules with inner diameter of 7–8 mm and 1 mm wall thickness. Thus, efficiency heat is 30–50% of the total heat evolving in the calorimeter. The efficiency heat can be determined as the difference of experiments performed for ampoules with samples and without. The ampoule is installed in the gradient-less zone of a furnace (0.2 K per 50 cm), the accuracy of thermodynamic temperature measurements being 0.3–0.5 K. The duration of the ampoule exposure in the furnace depends on how fast the heat equilibrium was attained. In our case it was 20–25 min. The heat losses upon the sample transfer from the furnace to the calorimeter did not exceed 0.5%. The calorimetric cell (massive copper block thermostated at 298.15 K) was screened from the furnace by special movable shutters. Temperature fluctuations in the thermostat did not exceed 0.002 K (the thermometer circuit sensitivity was $4 \cdot 10^{-5}$ K). The average duration of main period was 15–20 min. The Pfaundler correction for the heat exchange did not exceed 5% of the overall temperature raise in the cell. Since the spread of the calorimeter cooling constants was about 7% and the error of the heat equivalent determination was 0.15%, the overall error of heat measurement was less than 0.7%. The calorimeter calibration with respect to standards (α-Al_2O_3 and mercury) gave the random spread of 0.5%.

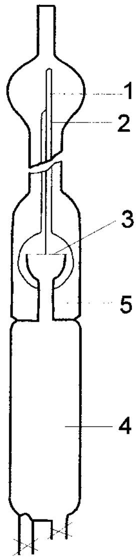

Fig. 1 Quartz membrane zero-manometer.
1 – the moving stock; 2 – the basic stock; 3 – the sensor element; 4 – the working cell; 5 – the compensative part.

When the measurements being completed, the ampoule was transferred into the furnace heated to a new temperature with a special device. This equipment essentially improved the efficiency of a calorimeter.

The pressure of saturated and unsaturated vapours was measured by the static method using quartz membrane zero manometers of the Novikov-Suvorov construction [13]. These manometers have the same or even higher sensitivity as those used by *Oppermann* [14], their sensor area being much smaller. This factor decreases elastic and inelastic deformation always arising in a glass at the high temperature change. Fig. 1 presents the draft of the device used.

First, this device with both sides opened to atmosphere, was installed in the furnace and the calibration experiment was carried out to determine the corrections for the temperature drift of zero position of the moving stock. Such corrections did not exceed 1.5 ± 0.1 Torr (1 Torr = 133,32 Pa). The loading of the device with the substance under study was performed as described elsewhere [14].

Before loading the device was heated for 4 hours under high vacuum at 1000–1100 °C to remove moisture and other substances. During the measurements the zero manometer was thermostated. The accuracy of the temperature maintenance was 0.2 K.

The maximum temperature drop in the device did not exceed 2 K at 1200 K. The error of the temperature measurement estimated from experiments with nitrogen and mercury was ± 1 K at 600 K and increased to 2 K at 1200 K. The pressure measurement error including compensation errors and the zero position determination errors was less than 0.3 Torr.

Experimental Results

In this work we used following expression for temperature function of heat capacity:

$$Cp = A \cdot T^{-2} + B \cdot T^{-1} + C + D \cdot T + E \cdot T^2.$$

For the substance under consideration some terms were statistical negligible.

The enthalpy temperature dependencies for the InI_2 low temperature modification (InI_2, crII) were measured in 24 calorimetric experiments at the temperature range of 346–421 K.

Results were approximated by the following expression:

$H^0(T) - H^0\ (298.15) = -18100 + 37.35 \cdot T$
$+ 0.1016 \cdot T^2 - 0.7803 \cdot 10^{-4}\ T^{-3}$ J/mol.

Thus, $C^0_p(T) = 37.35 + 0.2032 \cdot T - 0.2341 \cdot 10^{-3} \cdot T^2$ J/mol/K

17 measurements of the high temperature InI_2,cr enthalpy at 434–488 K give:

$H^0(T) - H^0\ (298.15) = 24520 - 134.6 \cdot T + 0.2453 \cdot T^2$ J/mol
and
$C^0_p(T) = 0.4906 \cdot T - 134.6$ J/mol/K

For the liquid InI_2 15 measurements at 499–684 K give:

$H^0(T) - H^0\ (298.15) = 96.11 \cdot T + 0.01577 \cdot T^2 - 21820$ J/mol;
$C^0_p(T) = 96.11 + 0.03154 \cdot T$ J/mol/K;
$\Delta_{tr}H^0\ (InI_2,\ 428\ K) = 1.5 \pm 0.2$ kJ/mol
$\Delta_m H^0\ (InI_2,\ 497\ K) = 11.6 \pm 0.3$ kJ/mol

It should be noted that we have met some kinetic restrictions when studying thermodynamic characteristics of the diiodide transition crII → crI.

We also studied the InI_3, crI-“yellow” phase (28 measurements at 335–480 K) and liquid triiodide (34 measurements, 483–723 K). For InI_3,crI we obtained:

$H^0(T) - H^0\ (298.15) = -32\,720 + 123.4 \cdot T - 0.0701 \cdot T^2$
$+ 0.8206 \cdot 10^{-4}\ T^3 \cdot$ J/mol;
$C^0_p(T) = 123.4 - 0.1402 \cdot T + 2.462 \cdot 10^{-4}\ T^2 \cdot$ J/mol · K

For InI_3, liq we obtained:

$H^0(T) - H^0\ (298.15) = -224900 + 0.05884 \cdot T^2 + 4.035 \cdot \ln T$ J/mol;
$C^0_p(T) = 0.1177 \cdot T + 40350/T$ J/mol

The equilibrium of gas phase with liquid InI_3 was studied by the static method. Four series of experiments were performed, varying the ratio sample weight to volume from 0.2 to 40 g/l, the temperature from 477 K to 674 K. Data analysis on saturated vapor shows that under the examined conditions the pressure does not depend on initial concentrations. Thus, at InI_3 evaporation the equilibrium is monovariant. The data of all four series (81 experimental points) can be approximated by the following expression:

$\ln(P/P^0) = 13.723 - 10130/T \pm 2\sigma$,
where $\sigma^2 = 0.000700 - 0.872/T + 272/T^2$ (477–674 K)

For this and following expressions $P^0 = 1$ atm = 760 Torr = 101.325 kPa.

The approximation was connected with minimization of the following function [23]:

$Y = \Sigma(P_e - P_c)^2/W$

where P_e – experimental value of the pressure, P_c – calculated value, W – statistical weight of the experimental point. The maximal difference between the total pressure values was –1.4 Torr at P(tot) = 200 Torr and T = 673 K (Fig. 2).

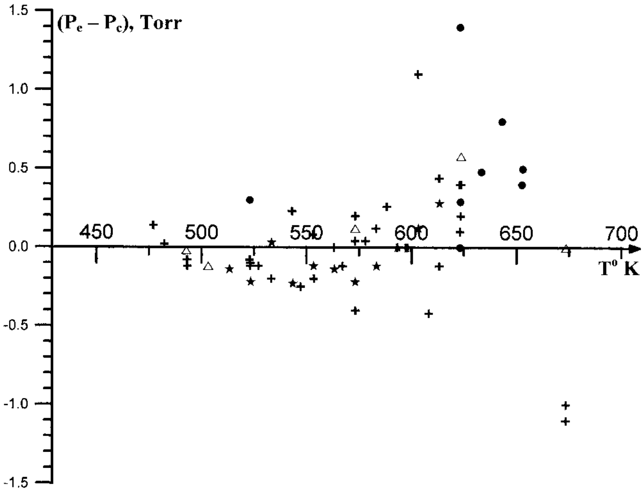

Fig. 2 The difference between the experimental and calculated from the regression expression values of total pressure for the saturated vapour of the liquid InI_3 as the temperature function at the different InI_3 concentration, C mol · cm^{-3} + – 0.80 · 10^{-4}; Δ – 0.13 · 10^{-4}; • – 0.40 · 10^{-5}; ★ – 0.64 · 10^{-5}.

As for unsaturated vapor the average gas molecular mass greatly decreases if the temperature is increased. For example, for the initial concentration of 0.64 · 10^{-3} mol/l the molecular mass was changed from 600 (680 K) to 433 (1173 K) ($M_{InI_3} = 495.53$). So, the polymerization and dissociation processes occur in the equilibrium gas phase.

At studing the evaporation processes of InI_2 it was found that the saturated vapor pressure was not constant at constant temperature but depended on the initial InI_2 concentration. Increasing the ratio of the sample weight to volume, we could find the conditions at which the solution composition changed insignificantly. 4 measurement series (75 points, concentra-

Table 2 Pressure concentration dependence over InI–InI_3 melts as a function of temperature at 520–830 K. Approximation accuracy (ΔP/P) was 5% for 520 K and 0.5% for 800 K.

Composition InI_x	Number of points	$\ln P/P^0 = A - B/T$[a]) A	B
2.103	12	11.26	9526
2.088	13	11.53	9841
2.082	15	11.55	9857
2.077	28	11.74	10027
2.073	17	11.72	10037
2.061	10	11.91	10244
2.038	10	12.09	10496
2.026	7	12.36	10870
1.816	8	12.37	11690
1.683	4	11.53	11270

[a]) P^0 = 1 atm = 101,325 kPa

tions ranged from 50 to 100 g/l) can be approximated by the following expression:

$\ln(P/P^0) = 11.562 - 10524/T \pm 2\sigma$,
where $\sigma^2 = 0.00266 - 4.101/T + 1590/T^2$ (523–843 K)

In special experimental series we also studied how the pressure over InI–InI_3 solutions depends on the concentration.

Table 2 presents the results obtained.

Interpolation the data of Table 2 to $x = 2$ gives equation: $\ln(P/P^0) = 12.34 - 10980/T$
This equation agrees well with the measurements over liquid InI_2.

Discussion

Earlier the same samples were studied by electronographic method [9] and low temperature calorimetry [15–17]. The structure and the atom–atom distances for the gas indium iodides were determined in [9]. Besides set of frequencies of vibration was recommended in this publication. The low temperature calorimeter measurements were performed in range from 7 to 300 K [15–17]. The data [9, 15–17] obtained gave information on the heat capacities and absolute entropies of the gas phase (model: harmonic oscillator – rigid rotator) and condensed indium iodides:

$C^0_p(\mathrm{InI,g}) = 37.40 - 0.418 \cdot 10^5\ T^{-2}$,
$S^0_{298}(\mathrm{InI,g}) = 267.2 \pm 1.0$ J/mol/K

$C^0_p(\mathrm{InI_3,g}) = 83.10 + 2.978 \cdot 10^{-5}\ T - 17710 \cdot T^{-2}$,
$S^0_{298}(\mathrm{InI_3,g}) = 401 \pm 4$ J/mol/K

$C^0_p(\mathrm{In_2I_6,g}) = 182.9 - 3.594 \cdot 10^{-5}\ T - 306500 \cdot T^{-2}$,
$S^0_{298}(\mathrm{In_2I_6,g}) = 655.6 \pm 8$ J/mol/K

$C^0_p(\mathrm{In_2I_4,g}) = 131.3 + 1.216 \cdot 10^{-4}\ T - 383600\ T^{-2}$,
$S^0_{298}(\mathrm{In_2I_4,g}) = 512.5 \pm 10$ J/mol/K

$C^0_p(\mathrm{InI,cr}) = 58.10 - 0.03708 \cdot T + 70.59\ 10^{-6}\ T^2$ (298–637 K)
$S^0_{298}(\mathrm{InI,cr}) = 119.9 \pm 0.2$ J/mol/K [14]

$S^0_{298}(\mathrm{InI_2,crII}) = 173.6 \pm 0.4$ J/mol/K [16]
$S^0_{298}/\mathrm{InI_3,crI}) = 223.0 \pm 0.4$ J/mol/K [17]

The study of the unsaturated vapor pressures within wide temperature and concentration ranges in the In–I system [18] (these data are consistent with results [9]) allowed us to obtain thermodynamic characteristics of processes occurring in the gas phase:

In_2I_6,g = 2 InI_3,g (1)

InI_3,g = InI,g + I_2,g (2)

In_2I_4,g = InI,g + InI_3,g (3)

$\Delta_{r1}H^0$ (298.15) = 102.1 ± 0.9 kJ
$\Delta_{r1}S^0$ (298.15) = 147.2 ± 1.2 J/K

$\Delta_{r2}H^0$ (298.15) = 193.6 ± 3.8 kJ
$\Delta_{r2}S^0$ (298.15) = 127.9 ± 3.3 J/K

$\Delta_{r3}H^0$ (298.15) = 137.4 ± 1.8 kJ
$\Delta_{r3}S^0$ (298.15) = 154.6 ± 1.9 J/K

Data processing [18] was performed using the above heat capacities and including the dissociation reaction of molecular iodine [19]. Taking into account the reaction characteristics (1) and (2) we can write the following expression for the partial pressures of InI_3 and In_2I_6 in equilibrium with liquid triiodide indium:

InI_3,liq = InI_3,g (4)

$\ln(P/P^0) = -59.415 - 33373/T - 10650/T^2$
$+ 9.9946 \cdot \ln T - 0.007076 \cdot T + 4852.9 \cdot \ln T/T$, (477–674 K)

Extrapolation gives:

$\Delta_{r4}H^0$ (298) = 108.07 ± 0.13 kJ
$\Delta_{r4}S^0$ (298.15) = 163.8 ± 0.9 J/K

For the process:

2 InI_3,liq = In_2I_6,g (5)

$\ln(P/P^0) = -149.93 - 53890/T - 18431/T^2 + 21.993$
$\cdot \ln T - 0.014153 \cdot T + 9705.8 \cdot \ln T/T$, (477–674 K)

$\Delta_{r5}H^0$(298) = 114.05 ± 0.95 kJ
$\Delta_{r5}S^0$ (298.15) = 180.4 ± 1.5 J/K

In a similar way we obtained for the congruent transition process of liquid diiodide into vapor:

2 InI_2,liq = In_2I_4,g (6)

$\Delta_{r6}H^0$ (497) = 104.5 ± 7.5 kJ
$\Delta_{r6}S^0$ (497) = 92.8 ± 2.8 J/K

Taking into consideration the temperature dependencies of the phase heat capacities and the enthalpies of the phase transitions for the diiodide sublimation process we can write:

2InI_2,crII = In_2I_4,g (7)

$\Delta_{r7}H^0$ (298.15) = 137.9 ± 8.0 kJ
$\Delta_{r7}S^0$ (298.15) = 164.0 ± 3.0 J/K

Earlier [24] the thermodynamic characteristics of the vapourisation process of indium monoiodide were investigated. It is monovariant equilibrium (M(experimental) = 239.5 ± 2.7; M(theory) = 241.72):

InI, liq = InI, g (8)

According [24] $C^0_p(\mathrm{InI,liq}) = 69 \pm 2$ J/mol/K (640–940 K)

For reaction (8):

$\Delta_{r8}H^0$ (637.5 K) = 106.2 ± 0.2 kJ/mol
$\Delta_{r8}S^0$ (637.5 K) = 107.05 ± 0.25 J/mol/K

The above experimental data allow us to determine thermodynamic characteristics for condensed phases and gas species by means of several thermodynamic cycles. For example, we can calculate the absolute entropy of gaseous InI_3 as:

$$\begin{aligned} S^0(InI_3,g) &= S^0(InI_3,crII) + \Delta_{tr}S^0(InI_3,crII) \\ &\quad + \Delta_m S^0(InI_3,crI) + \Delta_{r4}S^0 \\ &= S^0(InI_3,crI) + \Delta_m S^0(InI_3,crI) + \Delta_{r4}S^0 \\ &= (S^0(In_2I_6,g) - \Delta_{r1}S^0)/2 \\ &= S^0(I_2,g) + S^0(InI,g) - \Delta_{r2}S^0 \\ &= S^0(In_2I_4,g) - S^0(InI,g) + \Delta_{r3}S^0 \end{aligned}$$

Moreover, we can compare this value with that calculated from molecular constants according to the model "harmonic oscillator – rigid rotator" and can determine the absolute entropies of gaseous InI, In_2I_4, In_2I_6 by means of various thermodynamic cycles. We can design the similar cycles to determine the formation enthalpies of indium iodides using the calorimetry data on the direct synthesis of these compounds [20, 21]:

$In(cr) + 1.5\ I_2(cr) = InI_3(crI) \quad \Delta H^0_{298} = -223.9 \pm 0.6$ kJ

$InI(cr) + I_2(cr) = InI_3(crI) \quad \Delta H^0_{298} = -121.9 \pm 0.3$ kJ

$InI_2(crII) + 0.5\ I_2(cr) = InI_3(crI) \quad \Delta H^0_{298} = -47.7 \pm 1.3$ kJ

$InI_3(crII) = InI_3(crI) \quad \Delta H^0_{298} = 5.0 \pm 0.2$ kJ

$In(cr) + 0.5\ I_2(cr) = InI(cr) \quad \Delta H^0_{298} = -102.9 \pm 1.3$ kJ

$In(cr) + 1.5\ I_2(cr) = InI_3(crI) \quad \Delta H^0_{298} = -224.3 \pm 0.8$ kJ

$In(cr) + 1.5\ I_2(cr) = InI_3(crII) \quad \Delta H^0_{298} = -219.5 \pm 1.4$ kJ

Table 3 Standard formation enthalpies and absolute entropies of indium iodides

Composition	Phase	$\Delta_f H^0$ (298.15) kJ/mol	S^0 (298.15) J/mol/K
InI	cr	–102.5 ± 0.2	120.1 ± 0.1
InI	g	26.4 ± 0.5	268.1 ± 0.5
InI_2	crII	–176.0 ± 0.4	173.9 ± 0.4
In_2I_4	g	–215 ± 9.0	511.8 ± 8.4
InI_3	crII	–229.2 ± 0.6	205.4 ± 0.5
InI_3	crI	–224.0 ± 0.2	223.0 ± 0.4
InI_3	g	–105.4 ± 1.5	402.0 ± 2.0
In_2I_6	g	–311.9 ± 7.9	650.1 ± 8.5

Table 4 Characteristics of phase transitions of the In–I system compounds

Composition	Type of transition	T, K	P(atm)	ΔH^0, kJ
InI	cr → l	637.5	9.08×10^{-4}	17.26 ± 0.25
InI	l → InI(g)	637.5	9.08×10^{-4}	105.12
InI_2	crII → crI	428.1	1.59×10^{-8}	1.29 ± 0.21
InI_2	crI → In_2I_4	428.1	0.59×10^{-8}	130.62
InI_2	crI → InI_3(g) + InI(g)	428.1	1.00×10^{-8}	265.02
InI_2	crI → l	497.2	2.60×10^{-6}	11.85 ± 0.35
InI_2	2l → In_2I_4(g)	497.2	$0.90 \cdot 10^{-6}$	103.64
InI_2	2l → InI_3(g) + InI(g)	497.2	1.70×10^{-6}	237.19
InI_3	crII → crI	291.5	1.27×10^{-12}	5.16 ± 0.05
InI_3	crI → InI_3(g)	291.5	1.26 ± 10^{-12}	118.71
InI_3	2crI → In_2I_6(g)	291.5	0.01×10^{-12}	136.31
InI_3	crI → l	480.2	2.60×10^{-4}	18.48 ± 0.24
InI_3	l → InI_3(g)	480.2	2.10×10^{-4}	95.55
InI_3	2l → In_2I_6(g)	480.2	0.50×10^{-4}	93.13

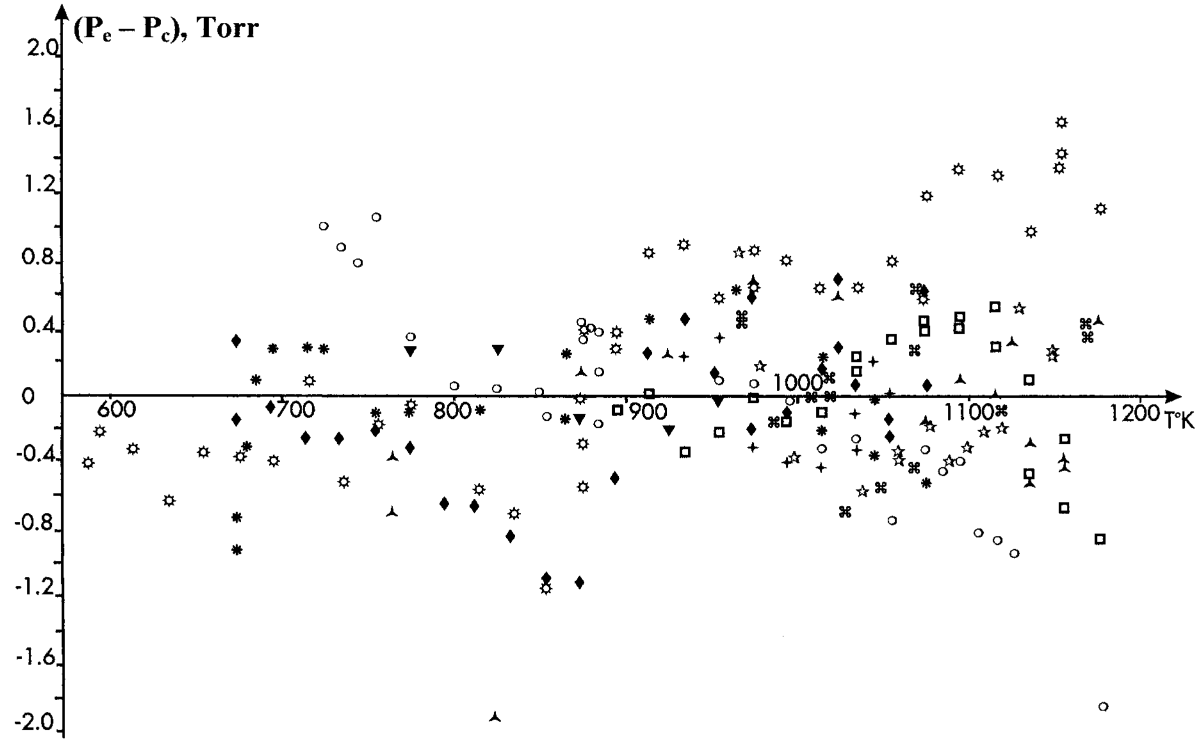

Fig. 3 The difference between the experimental and calculated according to the mutual consistent sets of the thermodynamic data values of total pressure for the unsaturated vapour for the In–I system as the temperature function at the different concentration ($C\ mol \cdot cm^{-3}$) of In and I, correspondently. ❍ – $0.5917 \cdot 10^{-5}$, $0.9187 \cdot 10^{-5}$; ✡ – $0.5956 \cdot 10^{-5}$, $0.9267 \cdot 10^{-5}$; ✦ – $0.4378 \cdot 10^{-5}$, $0.5846 \cdot 10^{-4}$; ⌘ – $0.3643 \cdot 10^{-5}$; $0.7031 \cdot 10^{-5}$; ▼ – $0.4088 \cdot 10^{-5}$, $1.2264 \cdot 10^{-5}$; ⅄ – $0.6403 \cdot 10^{-5}$, $1.9209 \cdot 10^{-5}$; ♦ – $0.1267 \cdot 10^{-4}$, $3.8010 \cdot 10^{-4}$; ✰ – $0.6245 \cdot 10^{-5}$, $2.0625 \cdot 10^{-5}$; ☐ – $0.1412 \cdot 10^{-5}$, $0.8358 \cdot 10^{-5}$; ❋ – $0.6083 \cdot 10^{-6}$, $0.4786 \cdot 10^{-5}$.

It should be noted that all the calorimetric data of papers [20, 21] were obtained on samples identical to those used in this study. It allow us to avoid possible systematic errors related to procedures of the sample preparation and pretreating. The calculation of the same characteristics (e.g. absolute entropy and enthalpy of formation for InI_3) via various thermodynamic cycles showed that, within the accuracy of measurements, the values obtained were in a good agreement. So, we can use the least square method to obtaining the recommended characteristics of indium iodides. (Under recommended characteristics we mean the formation enthalpies of gas species and condensed phases, that are most stable at P = 1 atm and T = 298.15 K). Moreover, the data on polymorph transitions and melting of substances are included here as well. Using these values we can calculate all the other thermodynamic characteristics of physico-chemical processes.

Thermodynamic values measured experimentally cannot always be considered as independent. For example, the experimental values of the evaporation entropy and enthalpy are correlated to each other. So, to obtain the consistent set of recommended characteristics we used the estimation procedure of parameters of models with several dependent variables [22]. According to this procedure one should minimize the following function:

$$\psi \qquad {}_{t\ 1\ s\ 1} \qquad y_{Et} \quad y_{Ct}\ \sigma^{ts}\ y_{Es} \quad y_{Cs}$$

are y_E experimental values of thermodynamic characteristics of physico-chemical processes, y_c – the values calculated over a set of recommended values, **t** or **s** is the item No of the value observed in the experiment (t, s = 1, …,   ), σ^{ts} – the element of matrix reverse to covariant matrix:

$$A \qquad \begin{matrix} \sigma_{11} & \sigma_{1} \\ \sigma_{\ 1} & \sigma \end{matrix}$$

Diagonal coefficients of the A-matrix are determined by the estimates of experimental value dispersions, nondiagonal coefficients equal zero for independent observations and can be calculated from correlation coefficients in other cases [22]. Table 3 and 4 present the mutual consistent sets of data on thermodynamic characteristics of indium iodides. The maximal difference between experimental and calculated values of total pressure of unsaturated vapour is 1.8 Torr at P(tot) = 170 Torr, vapour density = 0,0036 mol/l for mixture $InI_3 + 2.5\, I_2$ and T = 1180 K (Fig. 3).

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