

Enthalpies of formation of BaPdS₂ and LaPd₃S₄

A.A. Zubkov^{1,*}, T. Fujino, Y. Waseda, N. Sato, K. Yamada

Institute for Advanced Materials Processing, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980, Japan

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Abstract

The BaPdS₂ mixed palladium sulfide has been synthesized by direct reaction of a stoichiometric mixture of the PdS and BaS binary constituent sulfides. The standard molar enthalpies of formation of BaPdS₂ and LaPd₃S₄ mixed sulfides were determined by the method of direct reaction calorimetry through synthesizing the respective compounds in a calorimetric cell from the stoichiometric mixture of appropriate starting materials. Combining the experimental results with the reference data for the starting materials, we found $\Delta_{f,298}H_m^0(\text{BaPdS}_2) = -515.4 \pm 16.8 \text{ kJ mol}^{-1}$; and $\Delta_{f,298}H_m^0(\text{LaPd}_3\text{S}_4) = -817.6 \pm 43.8 \text{ kJ mol}^{-1}$. © 1998 Elsevier Science B.V.

Keywords: Barium palladium mixed sulphide; Palladium sulphide bronze ; Direct reaction calorimetry; Enthalpy of formation

1. Introduction

The binary and higher palladium sulfides is a widely studied class of materials with considerable technological interest (catalysts, acid resistant high-temperature electrodes, etc.), because of their special physico-chemical properties. In recent years, a number of studies on preparation and structural characterization of new palladium and other platinum-family metals mixed sulfides and sulfide bronzes has been carried out [1–4]. However, no data on the thermodynamic properties of these compounds have been reported till now. At the same time, when these data become available, it helps in optimizing the conditions of both preparation and technological application of these sulfides, and

possibly gives better understanding of the potential areas for synthesizing new related compounds.

In our previous publication, we represented the results of thermochemical study of the binary palladium sulfides [5]. In the present research, we report the enthalpies of formation for two recently synthesized compounds: the BaPdS₂ barium palladium mixed sulfide [1] and the LaPd₃S₄ palladium sulfide bronzes [2–4]. The thermodynamic data were received by a direct reaction calorimetry method through synthesizing the phase in question from the stoichiometric mixture of appropriate starting materials in the calorimetric cell.

2. Experimental

2.1. Materials

The starting materials used in this study were lumps of elemental sulfur from Kanto Chemicals (lot# 172;

*Corresponding author. Tel.: 001 416 663 5120; e-mail: zubkov@front.net

¹Visiting Scientist. Current address: Department of Metallurgy and Materials Science, University of Toronto, 184 College Street, Toronto, ON M5S 3E4, Canada.

>99.9 wt% purity); palladium powder from Tanaka Kikinzoku Kogyo K.K. (200 mesh; lot# 611-001; 99.990 wt% purity); BaCO₃ from Wako Pure Chemical Industries (lot# LKE 2494; assay 99.0–100.3 wt%); La₂O₃ from Michigan chemical (lot# La103-0; 99.99 wt% purity); CS₂ from Wako pure chemicals (lot# DLF 7497; 99.0 wt% purity), was used as a source of sulfur in the reaction of the preparation of BaS and La₂S₃; and N₂ gas from Nippon Sanso (99.9 vol% purity), was used as a carrier gas for the CS₂.

Palladium monosulfide was prepared by direct reaction of a stoichiometric mixture of the elements. Elemental sulfur was ground and intimately mixed with palladium powder in an agate mortar for ca. 1 h. The mixture was pressed at ca. 3×10^8 Pa by a uniaxial press to form a 10 mm diameter pellet which was annealed in an evacuated fused silica ampoule at 873 K for 27 h. After intermediate grinding, the powdered sample was annealed at 773 K for 43 h and quenched into water within the ampoule. No indication for reaction between the samples and silica during the heat treatment was observed. No traces of unreacted sulfur precipitated on the inner walls of the ampoule after quenching.

An X-ray diffraction analysis of all the samples, in the present study, was carried out with the help of Rigaku RAD-IC diffractometer using CuK_α ($\lambda=1.54056$ Å) radiation (40 kV, 20 mA) monochromatized with curved pyrolytic graphite. X-ray powder diffraction pattern of the sample of the synthesized PdS compared with that available in literature [6] and the one calculated from structural parameters [7] revealed a single phase structure.

Barium sulfide was prepared by the reaction of BaCO₃ with gaseous CS₂ in the N₂ carrier gas. The gas mixture of CS₂ and N₂ was obtained by passing the N₂ gas through a bubbler containing liquid CS₂ at room temperature. The flow rate of N₂ was measured using Kasano FT-1/1,6-14-150 float flowmeter. The concentration of CS₂ in the gas mixture was calculated from the volume change of CS₂ in the bubbler. The powder of starting carbonate was suspended at 500 K in an 100–120 ml min^{−1} stream of nitrogen for ca. 30 min and then at 1123 K in a 50/100 ml min^{−1} stream of the CS₂/N₂ gas mixture for 3 h. X-ray powder diffraction pattern of the gray powder after the treatment, compared with that available in litera-

ture [8] and the one calculated from structural parameters [7], revealed a single phase structure. As the sulfide is reported to be moisture-sensitive [9], the freshly prepared compound was put and stored under protection atmosphere of pure N₂.

Lanthanum sesquisulfide was prepared by the reaction of La₂O₃ with gaseous CS₂ in the N₂ carrier gas in a similar way to that of the BaS sulfide. The powder of starting oxide was suspended at 1173 K in a 50/100 ml min^{−1} stream of the CS₂/N₂ gas mixture for 3 h. X-ray powder diffraction pattern of the sample compared with that calculated from structural parameters [7] revealed a single phase structure.

2.2. Apparatus, atmosphere, calibrations

The calorimetric experiments were carried out with the help of a high precision heat-flow calorimeter designed and built up in Multiphase Processing Laboratory, Institute for Advanced Materials Processing, Tohoku University. A detailed description of the apparatus design, performance and calibration procedures have been reported recently [5,10].

The calorimetric detector of the apparatus is shown in an exploded view in Fig. 1. The detector assembled on a machined ceramic tube (CT) consists of twenty (Pt-Pt+Rh) thermocouples constructed from Pt strips (PS) and Pt+Rh contact wires (PRW). The strips are positioned vertically on the inner surface of the tube and the wires are arranged on its outer surface. The latter are led through holes into the tube and spot welded to the middle of each strip near its upper edge to form a working junction (WJ) and near its lower edge to form a reference junction (RJ). The wire attached to the upper part of one strip is connected to the lower part of the next strip. The upper part of the latter strip is connected by the wire with the lower part of the next strip and so on to form a thermopile. The pieces of the wire attached to the lower part of the first strip and the upper part of the last one are led outside. The WJs of this thermopile positioned at four different levels are distributed over the 'working area' where the working crucible (WC) is mounted. All the RJs are arranged at the same level, some distance below the WJs. The calorimetric detector surrounded by platinum radiation shield (PSH) is positioned vertically in a cylindrical well of 130 mm height and 80 mm diameter massive Inconel 600 jacket (IJ) as illustrated

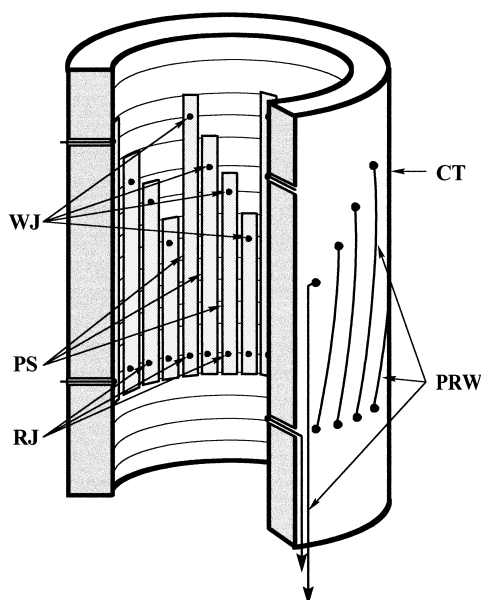


Fig. 1. Exploded view of the measuring element: CT, machined ceramic tube; PS, platinum strips; PRW, platinum–rhodium contact wires; WJ, working junctions; RJ, reference junctions.

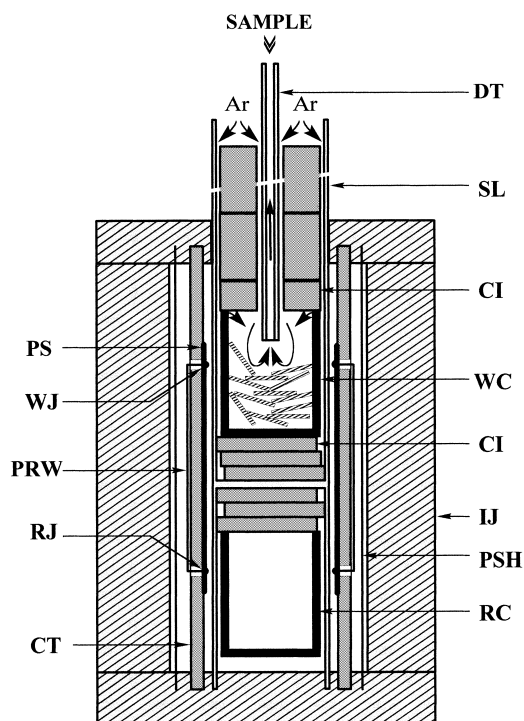


Fig. 2. General layout of the calorimeter assembly: DT, quartz tube guiding drops of samples; SL, silica liner; CI, ceramic insulators; WC, working crucible; IJ, Inconel jacket; PSH, platinum radiation shield; RC, reference crucible; PS, platinum strips; WJ, working junctions; PRW, platinum–rhodium contact wires; RJ, reference junctions; CT, machined ceramic tube.

in Fig. 2. The calorimetric block assembly is placed within the uniform temperature zone of a heat resistant furnace. The output of the thermopile is fed in parallel to both a chart recorder and a circuit leading to an SP4400 ChromJet Computing Integrator adjusted to the conditions of the calorimetric experiments.

Working crucible (WC) and a reference crucible (RC) of the same size (ca. 18 mm outer diameter and 30 mm height) are arranged vertically and coaxially inside an 18.5 mm inner diameter removable silica tube 'silica liner' (SL) analogous with that used in Ref. [11]. The WC is thermally insulated from its top and bottom by a series of ceramic insulators (CI). We used platinum crucibles for the experiments with the sulfides containing barium, and alumina crucibles for the experiments with the sulfides containing lanthanum to avoid possible interaction between the samples and the crucible.

To empty or change the working crucible after each series of calorimetric experiments, the SL and its contents were slowly pulled out from the calorimetric block without switching off the power supply of the furnace. Before a next series of measurements the SL assembly was slowly inserted into the hot calorimetric

block. This made it possible to keep the calorimeter permanently at the same high temperature throughout a number of series of calorimetric experiments (during several months) and economize considerably the time necessary to recover a thermal equilibrium between the different series of calorimetric experiments.

To provide a complete envelope for the working crucible with its contents before each series of calorimetric experiments, the SL was flashed with a stream (ca. 100 ml min^{-1}) of high purity argon (99.9995 vol% purity) for 2 to 3 h. The inert gas flowed into the upper section of the 'silica liner' passed into the WC and flashed its content, then it came out through the tube guiding drop of samples (DT) as illustrated in Fig. 2. The gas flashing was stopped just before dropping samples containing sulfides to prevent sulfur to be flowed away from the samples by the outgoing stream of argon. No influence

of flashing on both level and stability of the base line was detected in the course of the reported experiments.

Calibration of the apparatus was carried out both before and after each series of calorimetric runs by dropping five to seven pieces of α - Al_2O_3 single crystals of 2.8 mm diameter and 70 to 110 mg weight from room temperature into the cell held at the temperature of the calorimetric experiments. The mass of the pieces of α - Al_2O_3 was chosen so as to produce approximately the same heat effects as those experienced by the samples under examination. The reference values [12] were used to calculate the enthalpy increment for α - Al_2O_3 in the temperature range concerned. The dependence of the calibration parameter on the amount of substance in the working crucible was checked by consecutive drops of ca. thirty pieces of α - Al_2O_3 (250 to 400 mg each) into the empty cell, i.e. the initially empty working crucible was gradually filled with the reference material. In all the cases, the calibration parameter was generally reproducible within $\pm 1\%$ (standard deviation) in the whole volume of the working crucible.

2.3. Calorimetric experiments

Enthalpies of formation of BaPdS_2 and LaPd_3S_4 at 298 K were measured by direct reaction technique through synthesizing the phases in question in the calorimetric cell from the stoichiometric mixture of appropriate initial substances. In all the cases, the powders of appropriate starting materials were intimately mixed for at least 40 min in an agate mortar under protection atmosphere of nitrogen in a glove box and pressed at ca. 3×10^8 Pa by a uniaxial press to form a 10 mm diameter pellet. The pellets were cut into seven to eight samples of 120 to 180 mg each. The samples kept at room temperature were dropped into the calorimetric cell held at 1073 K. This calorimetric procedure was consecutively performed twice for each sample. Completeness of transformation and absence of side processes (e.g. loss of sulfur) were checked by an X-ray diffraction examination, routinely carried out both after the first and the second series of calorimetric experiments. The total weight loss of the samples after the two drops did not exceed 0.2 wt%. No traces of precipitated sulfur were found after the calorimetric experiments on the inner surfaces of the SL.

2.3.1. BaPdS_2

This barium palladium mixed sulfide has been recently synthesized through reaction of $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ with a stream of dry H_2S at 870 K for 3 h or the reaction of $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ with sulfur in a slow, dry and oxygen-free argon stream (3 h at 870 K) [1]. In the course of the present study, we found that this mixed sulfide can also be prepared by a direct reaction between intimately mixed and pelletized PdS and BaS binary constituent compounds taken in a stoichiometric proportion. Preliminary experiments with the mixed and pelletized powders performed in sealed, evacuated fused-silica ampoules lined with pyrolytic carbon revealed that after 1 h treatment at 1073 K the samples only consisted of the BaPdS_2 phase. The powder X-ray patterns of the samples after the first and the second series of calorimetric experiments were compared with that of a sample annealed in the sealed evacuated silica ampoule at 1073 K overnight. No detectable differences were found between these X-ray patterns. In all the cases, the lattice parameters of the synthesized mixed palladium sulfide were in good agreement with those reported in the literature [1].

2.3.2. LaPd_3S_4

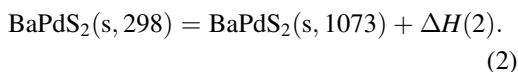
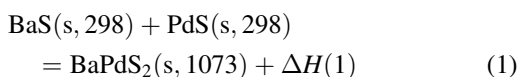
This palladium sulfide bronze has been recently synthesized by reaction of a stoichiometric mixture of the elements [2,3] or a mixture of the La_2S_3 sesquisulfide, pure palladium and sulfur [4]. In the present study, the La_2S_3 and PdS binary sulfides and pure palladium were chosen as starting materials for the direct reaction experiments. Preliminary experiments with the samples of the $\{1/2\text{La}_2\text{S}_3 + 5/2\text{PdS} + 1/2\text{Pd}\}$ pelletized stoichiometric mixture, carried out in sealed evacuated fused silica ampoules lined with pyrolytic carbon, revealed that after 1 h treatment at 1073 K ca. 20% of the sample remain unreacted. Annealing at higher temperatures yielded in less fraction of unreacted mixture (e.g. ca. 5% after 1 h treatment at 1103 K and <2% after 1 h treatment at 1173 K). However, because of considerable loss of sulfur during the calorimetric experiments with the unsealed samples at temperatures above 1073 K, the latter temperature was chosen for the calorimetric experiments with the $\{1/2\text{La}_2\text{S}_3 + 5/2\text{PdS} + 1/2\text{Pd}\}$ stoichiometric mixture. An X-ray diffraction analysis showed that the

mole fraction of the unreacted materials in the product and the lattice parameter of the formed LaPd_3S_4 were the same before and after the second calorimetric run. In all the cases, the lattice parameter of the sulfide bronze synthesized in the course of the calorimetric experiments was in good agreement with that reported in literature [3,4].

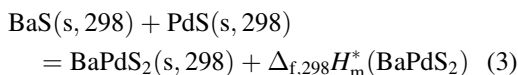
3. Results and discussion

3.1. Standard enthalpy of formation of the BaPdS_2 barium palladium mixed sulfide

Enthalpy of formation of BaPdS_2 from the BaS and PdS binary constituent sulfides at 298 K, $\Delta_{\text{f},298}H_{\text{m}}^*(\text{BaPdS}_2)$, was obtained from the heat effects of the following two reactions associated with the two consecutive drops of each sample:



Subtracting Eq. (2) from Eq. (1) gives us:

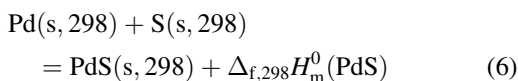
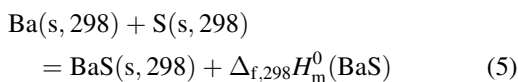


and so:

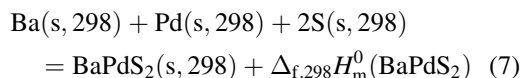
$$\Delta_{\text{f},298}H_{\text{m}}^*(\text{BaPdS}_2) = \Delta H(1) - \Delta H(2). \quad (4)$$

The measured heat effects associated with the first (a) and the second (b) drops of each sample are listed in Table 1 along with the values of $\Delta_{\text{f},298}H_{\text{m}}^*(\text{BaPdS}_2)$, calculated per 1 mol of BaPdS_2 . The latter value averaged from 11 separate pairs of measurements is positive and equals to $6.60 \pm 1.53 \text{ kJ mol}^{-1}$.

Combining reaction (3) with the reactions of formation of the binary constituent sulfides from the elements at 298 K:



gives the reaction:



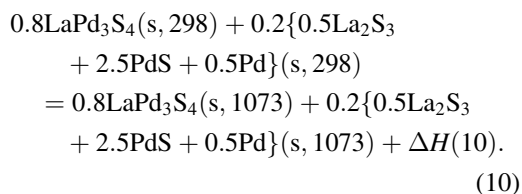
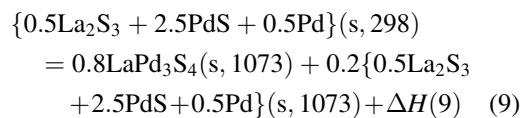
and so allows us to calculate the standard enthalpy of formation of this mixed sulfide:

$$\begin{aligned} \Delta_{\text{f},298}H_{\text{m}}^0(\text{BaPdS}_2) \\ = \Delta_{\text{f},298}H_{\text{m}}^0(\text{BaS}) + \Delta_{\text{f},298}H_{\text{m}}^0(\text{PdS}) \\ + \Delta_{\text{f},298}H_{\text{m}}^*(\text{BaPdS}_2). \end{aligned} \quad (8)$$

Using the reference data of $\Delta_{\text{f},298}H_{\text{m}}^0(\text{BaS}) = -443.9 \pm 12.6 \text{ kJ mol}^{-1}$ [13] and $\Delta_{\text{f},298}H_{\text{m}}^0(\text{PdS}) = -78.1 \pm 11.0 \text{ kJ mol}^{-1}$ [5], the value of $-515.4 \pm 16.8 \text{ kJ mol}^{-1}$ was obtained as the standard enthalpy of formation of the BaPdS_2 barium palladium mixed sulfide.

3.2. Standard enthalpy of formation of the LaPd_3S_4 palladium sulfide bronze

Enthalpy of formation of the LaPd_3S_4 palladium sulfide bronze from the $\{0.5\text{La}_2\text{S}_3 + 2.5\text{PdS} + 0.5\text{Pd}\}$ stoichiometric mixture at 298 K, $\Delta_{\text{f},298}H_{\text{m}}^*(\text{LaPd}_3\text{S}_4)$ was approximately calculated from the heat effects of the following two reactions associated with the two consecutive drops of each sample:



Since X-ray patterns of the samples were the same, before and after the second calorimetric runs, the reaction of the remaining starting materials associated with the second run was regarded as negligible. So the heat effects measured in the second runs were only associated with the enthalpy increment of the samples. Subtracting Eq. (10) from Eq. (9) gives us:

Table 1

Enthalpy of formation of the BaPdS₂ palladium mixed sulphide from the PdS and BaS binary constituent sulphides, $\Delta_{f,298}H_m^*$ (BaPdS₂) in kJ mol⁻¹

Experiment No.	$n\{\text{BaS}+\text{PdS}\}$ (mmol)	$\Delta H(1)$ (J)	$\Delta H(2)$ (J)	$\Delta_{f,298}H_m^*(\text{BaPdS}_2)$
1(a)	0.61954	52.78		4.45
1(b)			50.02	
2(a)	0.62869	54.93		5.50
2(b)			51.47	
3(a)	0.68271	60.48		6.94
3(b)			55.74	
4(a)	0.65481	57.42		5.60
4(b)			53.75	
5(a)	0.36513	32.73		8.24
5(b)			29.72	
6(a)	0.86199	77.61		5.23
6(b)	0.44421 ^a		37.67	
7(a)	0.23940	21.64		8.10
7(b)			19.70	
8(a)	0.63642	56.92		6.19
8(b)			52.98	
9(a)	0.49810	44.70		5.44
9(b)			41.99	
10(a)	0.35171	32.11		7.16
10(b)			29.59	
11(a)	0.76563	70.76		9.78
11(b)	0.41580 ^a		34.36	

^a A part of the sample was used for an X-ray analysis after the first drop.

$$\begin{aligned}
 &0.8\{0.5\text{La}_2\text{S}_3 + 2.5\text{PdS} + 0.5\text{Pd}\}(\text{s}, 298) \\
 &= 0.8\text{LaPd}_3\text{S}_4(\text{s}, 298) + \Delta H(9) - \Delta H(10).
 \end{aligned}
 \tag{11}$$

Pairs of the experimental data associated with the first (a) and the second (b) drops of each sample are represented in Table 2 along with the $(\Delta H(9) - \Delta H(10))$ difference calculated per 1 mol of the $\{0.5\text{La}_2\text{S}_3 + 2.5\text{PdS} + 0.5\text{Pd}\}$ stoichiometric mixture. The latter value averaged from four separate pairs of measurements is negative and equals to -9.2 ± 4.1 kJ mol⁻¹. After subtraction of Eq. (10) from Eq. (9), the term $0.2\{0.5\text{La}_2\text{S}_3 + 2.5\text{PdS} + 0.5\text{Pd}\}(\text{s}, 1073)$, representing the mole fraction of unreacted initial materials, is canceled from the left and right sides of reaction (11); we can then calculate an approximate value of $\Delta_{f,298}H_m^*(\text{LaPd}_3\text{S}_4)$ from the

difference of $(\Delta H(9) - \Delta H(10))$:

$$\Delta_{f,298}H_m^*(\text{LaPd}_3\text{S}_4) = \frac{(\Delta H(9) - \Delta H(10))}{0.8}.
 \tag{12}$$

The approximate value of $\Delta_{f,298}H_m^*(\text{LaPd}_3\text{S}_4)$ was found to be -11.5 ± 6.5 kJ mol⁻¹. Standard enthalpy of formation of the LaPd₃S₄ palladium sulfide bronze was calculated in a similar way to that of the BaPdS₂ phase. Using the approximate value of $\Delta_{f,298}H_m^*(\text{LaPd}_3\text{S}_4)$ along with the $\Delta_{f,298}H_m^0(\text{PdS}) = -78.1 \pm 11.0$ kJ mol⁻¹ [5] and $\Delta_{f,298}H_m^0(\text{La}_2\text{S}_3) = -1222 \pm 67$ kJ mol⁻¹ [13] reference data, an approximate value of the standard enthalpy of formation of the LaPd₃S₄ palladium sulfide bronze was calculated to be -817.6 ± 43.8 kJ mol⁻¹.

Table 2

Results of the calorimetric experiments with the $\{0.5\text{La}_2\text{S}_3+2.5\text{PdS}+0.5\text{Pd}\}$ stoichiometric mixture

Experiment No.	$n\{0.5\text{La}_2\text{S}_3+2.5\text{PdS}+0.5\text{Pd}\}$ (mmol)	$\Delta H(9)$ (J)	$\Delta H(10)$ (J)	$-(\Delta H(9)-\Delta H(10))$ (kJ mol ⁻¹)
1(a)	0.28220	41.11		13.54
1(b)			44.93	
2(a)	0.22374	32.40		9.83
2(b)			34.60	
3(a)	0.19973	29.26		10.91
3(b)			31.44	
4(a)	0.28587	41.68		2.55
4(b)			42.41	

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