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Enthalpy increments and enthalpies of formation of $Cd_{0.83}Ni_{0.17}$ and $Cd_{0.5}Ni_{0.5}$ intermetallic compounds

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Abstract

Cadmium is expected to be the solvent for pyrochemical processing of the burnt metallic nuclear fuel. Therefore, thermodynamic properties of cadmium with various fuel and clad elements are of interest. In the present paper enthalpy increments and enthalpies of formation of the two intermetallic compounds of Cd–Ni system, $Cd_{0.83}Ni_{0.17}$ and $Cd_{0.5}Ni_{0.5}$, are presented. Enthalpy increment data was acquired in the temperature range 375.15–713.55 K and 375.55–810.25 K, respectively, using a high temperature Calvet calorimeter and the drop technique. The enthalpies of formation of the two compounds at 298.15 K, obtained by tin solution calorimetry, were −8.14 kJ/mol and −18.64 kJ/mol, respectively.

Keywords: Alloys; Nuclear rector materials; Enthalpy; Calorimetry

1. Introduction

In the integrated fast breeder concept, burnt metallic fuel is expected to be processed by pyrochemical method using liquid cadmium as solvent [1]. To understand this process, knowledge of thermodynamic behaviour of all its constituents is very important. Nickel being one of the important constituents of clad is also expected to be present along with burnt fuel at the time of reprocessing. As limited thermodynamic information is available in literature on Cd–Ni system, calorimetric investigation of this system was undertaken.

The intermetallic compounds $Cd_{0.83}Ni_{0.17}$ and $Cd_{0.5}Ni_{0.5}$ melt peritectically and have narrow non-stoichiometric range of stability [2]. Enthalpy increments and enthalpies of formation of these two compounds was measured using high temperature Calvet calorimeter.

2. Experimental

The compounds $Cd_{0.83}Ni_{0.17}$ and $Cd_{0.5}Ni_{0.5}$ were prepared by directly heating the stoichiometric amounts of cadmium (purity 99.999%) and nickel (purity 99.998%) in a quartz capsule, sealed under argon, at 1273 K for 120 h. The alloy formation was confirmed by XRD [3,4]. Basically, two types of experiments were carried out with these compounds: (1) enthalpy increment measurements; and (2) enthalpy of formation measurements. Both types of measurements were carried out using high temperature Calvet calorimeter of Setaram. The instrument employed for these measurements has been described in detail previously [5]. For the sake of clarity, a short description of the instrument is presented here. The Calvet calorimeter is an isothermal calorimeter with massive blocks of alumina to maintain constant temperature. It has two cavities in the middle surrounded by identical Pt/Pt–Rh thermopiles capable of detecting heat change of 2.5 mJ. Two identical one end close alumina tubes were placed in these cavities. The alumina tubes were attached to a sample introducer which can be maintained at a constant ambient temperature, 298.15 K, using a water bath. The whole set-up was gas-tight.

The enthalpy increment ($\Delta H^{T}_{298.15\ K}$) measurements of the compounds $Cd_{0.83}Ni_{0.17}$ and $Cd_{0.5}Ni_{0.5}$ were carried out in the temperature range 375.15–713.55 K and 375.55–810.25 K, respectively. For these measurements, 7 cm long quartz tubes were placed in the alumina tubes. The whole set-up was evacuated and flushed with argon two to three times while heating it to the experimental temperature. Experiments were carried out under argon atmosphere (purity 99.999%) at 1 atm pressure. When the experimental temperature was attained and calorimeter

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attained equilibrium, the thermopile output became constant. At the equilibrium experimental temperature, the calorimeter was calibrated using an NBS standard reference material, synthetic sapphire. A weighed amount of the reference material was dropped from ambient temperature (298.15 K) into the calorimeter at experimental temperature. After four to five such calibration drops, weighed amounts of the intermetallic compounds were dropped at the same experimental temperature. These measurements were also repeated four to five times to confirm reproducibility of the data. The calibration data with alumina showed an average standard deviation of less than ±1%. Whereas, enthalpy increment data of the compounds showed a standard deviation of ±2–±5% at individual temperatures. The deviation was high (~±5%) for the compound $Cd_{0.5}Ni_{0.5}$, especially at high temperatures. Enthalpy increment values for the NBS standard reference material, synthetic sapphire (Al_2O_3), were taken from Ref. [6].

The enthalpies of formation of the compounds were determined by solution calorimetry. Liquid tin metal was used as the solvent. For these experiments, a large amount (7–10 gm) of tin metal was loaded in a quartz tube. The whole set-up was evacuated and flushed with argon three to four times. The instrument was then heated to the experimental temperature under an argon atmosphere. The experiments were carried out under a closed argon pressure of 1 atm. The system was calibrated by dropping weighed amounts of tin metal from ambient temperature, 298.15 K, into the tin bath at the experimental temperature. The corresponding heat changes were equivalent to enthalpy increments of the pure tin metal. For calibration, the enthalpy increment values for pure tin were taken from Hultgren et al. [7]. Experiments were carried out by dropping small weighed amounts of intermetallic compounds (0.02–0.03 gm) from 298.15 K to the tin bath at experimental temperature. The amount of the compounds dropped were maintained very small compared to tin metal to ensure infinite dilution of the compounds, $X_{Sn} \sim 1$. The calibration of the instrument was repeated at the end of the experiments by adding NBS standard, synthetic sapphire, from ambient temperature, 298.15 K, to the bath at experimental temperature. This indicated that the calibration factor in these experiments was independent of height. A similar set of experiments were repeated with pure nickel and cadmium metals to determine heat of solution of the constituent elements in tin metal added from 298.15 K to the same experimental temperature. The experimental temperature for heat of solution measurements for the compounds and the pure metals was 888.75 K. At the end of the experiments, small weighed amounts of pure tin metal were dropped from 298.15 K into the reaction crucible at 888.75 K. The observed heat change corresponded to the enthalpy increment of tin metal. This confirmed infinite dilution of the investigated component with tin. The reproducibility of the enthalpy of dissolution value was confirmed by repeating the whole dissolution experiment three to four times for the pure metals and both compounds.

3. Results and discussion

3.1. Enthalpy increments of $Cd_{0.83}Ni_{0.17}$ and $Cd_{0.5}Ni_{0.5}$ compounds

The enthalpy increment values measured at different temperatures were least square fitted in a polynomial equation using Microsoft Excel software, by fixing the value of $\Delta H^{T}_{298.15\ K}$ ($T = 298.15$ K) as zero. The equations thus derived are:

$$Cd_{0.83}Ni_{0.17}\text{: } \Delta H^{T}_{298.15\ K}\ (\mathrm{J/mol}) \pm 191 = -6943 + 21.661\ T + 0.0055\ T^2 \qquad (1)$$

$$Cd_{0.5}Ni_{0.5}\text{: } \Delta H^{T}_{298.15\ K}\ (\mathrm{J/mol}) \pm 172 = -7322 + 22.183\ T + 0.008\ T^2 \qquad (2)$$

where the errors given in Eqs. (1) and (2) are average standard deviations of the least square fit data from the experimental data.

Heat capacities of the two compounds derived from the above enthalpy increment equations are:

$$Cd_{0.83}Ni_{0.17}\text{: } Cp\ (\mathrm{J/K.mol}) = 21.661 + 0.011\ T, \qquad (3)$$

$$Cd_{0.5}Ni_{0.5}\text{: } Cp\ (\mathrm{J/K.mol}) = 22.183 + 0.016\ T. \qquad (4)$$

The enthalpy increment values, $\Delta H^{T}_{298.15\ K}$, of the two intermetallic compounds calculated from the least square fits given in Eqs. (1) and (2), are compared with experimental values in Tables 1 and 2.

3.2. Partial enthalpy of solution of cadmium in tin

The partial enthalpy of solution of cadmium in liquid tin ($\Delta\overline{H}^{o}_{sol,Cd}$) was reported as 7.28 kJ/mol at 598 K by Boom [8]. However, in the table of selected values of the partial

Table 1
A comparison of the experimental and calculated enthalpy increment values of $Cd_{0.83}Ni_{0.17}$

Temp. (K)	Exp. $\Delta H^{T}_{298.15\ K}$ (J/mol)	Calc. $\Delta H^{T}_{298.15\ K}$ (J/mol)
375.15	1862.1	1957.3
426.25	3310.4	3289.5
477.85	4862.2	4663.8
508.45	5276.0	5492.6
528.65	5896.7	6045.4
559.15	7345.1	6899.7
590.55	7655.4	7767.3
621.25	8483.0	8636.9
652.05	9310.6	9519.7
682.95	10 448.6	10 416.0
713.55	11 379.7	11 313.8

Table 2
A comparison of the experimental and calculated enthalpy increment values of $Cd_{0.5}Ni_{0.5}$

Temp. (K)	Exp. $\Delta H^{T}_{298.15\ K}$ (J/mol)	Calc. $\Delta H^{T}_{298.15\ K}$ (J/mol)
375.55	2324.7	2137.2
416.35	3182.5	3300.7
436.85	4082.4	3895.4
457.35	4390.9	4496.8
477.75	5052.6	5101.9
508.45	5890.6	6025.2
528.65	6703.0	6640.9
549.35	7385.8	7278.6
580.05	8217.3	8237.0
610.75	9119.0	9210.4
631.25	9888.6	9868.9
651.75	10 577.0	10 534.1
682.35	11 530.4	12 563.2
713.05	12 104.7	159 034.0
810.25	16 148.8	15 982.3

Table 3
Partial enthalpies of solution of cadmium in liquid tin. Cd (liq, T(K)) + Sn (liq, T(K)→Cd (Sn, T(K)) (∞ dilution)

References	Temp (K)	$\Delta\overline{H}^{o}_{sol,Cd}$ (kJ/mol)
Pool [9]	655	8.222
	700	7.322
	750	6.192
Orr et al. [10]	623	7.238
	723	6.736
Kleppa [11]	517	7.573
Darby et al. [12]	689	6.907
Hultgren [13]	773	6.577
Present value	888.75	29.45–23.15 = 6.3

enthalpy of solution given by the same author, the partial enthalpy of solution of liquid cadmium in liquid tin at 600 K is listed as 7.15 kJ/mol. Pool [9] has reported $\Delta\overline{H}^{o}_{sol,Cd}$ values as 8.22, 7.32 and 6.19 kJ/mol at 655, 700 and 750 K, respectively. Orr et al. [10] have reported it at lower temperature, 517 K, as 7.57 kJ/mol. Kleppa [11] has reported it at two temperatures, 623 and 723 K, as 7.24 and 6.74 kJ/mol, respectively. Darby et al. [12] have given a value of 6.91 kJ/mol at 689 K. Hultgren et al. [13] have given partial enthalpy of solution of cadmium in liquid tin at infinite dilution at 773 K as 6.58 kJ/mol. Hultgren et al. have calculated this value from selected Gibbs free energy data and enthalpy of mixing data using Gibbs–Duhem relation. The value given by Hultgren et al. is in general agreement with the reported literature data [8–12]. The enthalpy of solution data reported in literature ($\Delta\overline{H}^{o}_{sol,Cd}$) represents the enthalpy change due to dissolution of cadmium in liquid tin at infinite dilution, where both solute and solvent were kept at the same experimental temperature as that of solution. Whereas, the present experimental enthalpy of solution value 29.45 kJ/mol, at 888.75 K, represents the enthalpy change for addition of cadmium, at 298.15 K, into liquid tin at experimental temperature, 888.75 K. To compare present data with literature data, a partial enthalpy of solution of cadmium in liquid tin at 888.75 K ($\Delta\overline{H}^{o}_{sol,Cd}$) was calculated by subtracting enthalpy increment of cadmium ($\Delta H^{888.75\ K}_{298.15\ K}\underline{Cd} = 23.15$ kJ/mol) from the present experimental value ($\Delta\overline{H}^{o}_{sol,Cd}$ (298.15 K)). All these values are listed in Table 3. As shown in the Fig. 1, the partial enthalpy of solution values of Pool [9] show a higher negative gradient with respect to temperature, compared to that of Orr et al. [10], Kleppa [11], Darby et al. [12] and Hultgren et al. [13]. None of the previous partial enthalpy of solution data was reported at a temperature as high as 888.75 K. A linear extrapolation of Kleppa, Orr et al., Darby et al. and Hultgren et al. data to higher temperature showed that present partial enthalpy of solution value, 6.30 kJ/mol at 888.75 K, is in agreement with these literature values. The linear least square fit of literature data (excluding Pool [9] data) and present data as a function of temperature, using Microsoft Excel software, gives the following equation:

$$\Delta\overline{H}^{o}_{sol,Cd}(T)\ (kJ/mol) = 9.4006–0.0036\ T \qquad (5)$$

3.3. Partial enthalpy of solution of nickel in tin

The partial enthalpies of solution of liquid nickel in liquid tin at infinite dilution ($\Delta\overline{H}^{o}_{sol,Ni}$) reported by Hultgren [13] are listed in Table 4 at various temperatures. These values are in agreement with experimental data of Hertz [14], Oriani and Murphy [15], and Day and Hultgren [16]. Leach and Bever [17] have reported $\Delta\overline{H}^{o}_{sol,Ni}$ as −31.25 kJ/mol at 623.15 K on dissolution of metallic nickel added from 273.15 K in the liquid tin at 623.15 K. On subtracting enthalpy increment and enthalpy of fusion values of nickel from this value, partial enthalpy of solution of liquid nickel in liquid tin, (both maintained at 623.15 K) is −63.64 kJ/mol. Whereas, extrapolation of the values given by Hultgren et al. [13] to the temperature 623.15 K, gives a partial enthalpy of solution value −72.97 kJ/mol. Therefore, Leach and Bever value is 9.33 kJ/mol less exothermic than the accepted values of Hultgren et al. However, Hultgren et al. have reported a difference of 23.43 kJ/mol between their accepted value and the one reported by Leach and Bever. This discrepancy can be accounted by considering that Leach and Bever had added nickel from 273.15 K. Whereas, while calculating partial enthalpy of solution of liquid nickel in liquid tin at 623 K from the reported value of Leach and Bever, Hultgren et al. might have considered the enthalpy of fusion factor but not the enthalpy increment of nickel from 273.15 to 623.15 K. Day and Hultgren [16] have reported the partial enthalpy of solution of nickel in liquid tin at 910 K. They have carried out two sets of experiments, by adding nickel from 376.0 and 369.1 K into tin at 910 K,

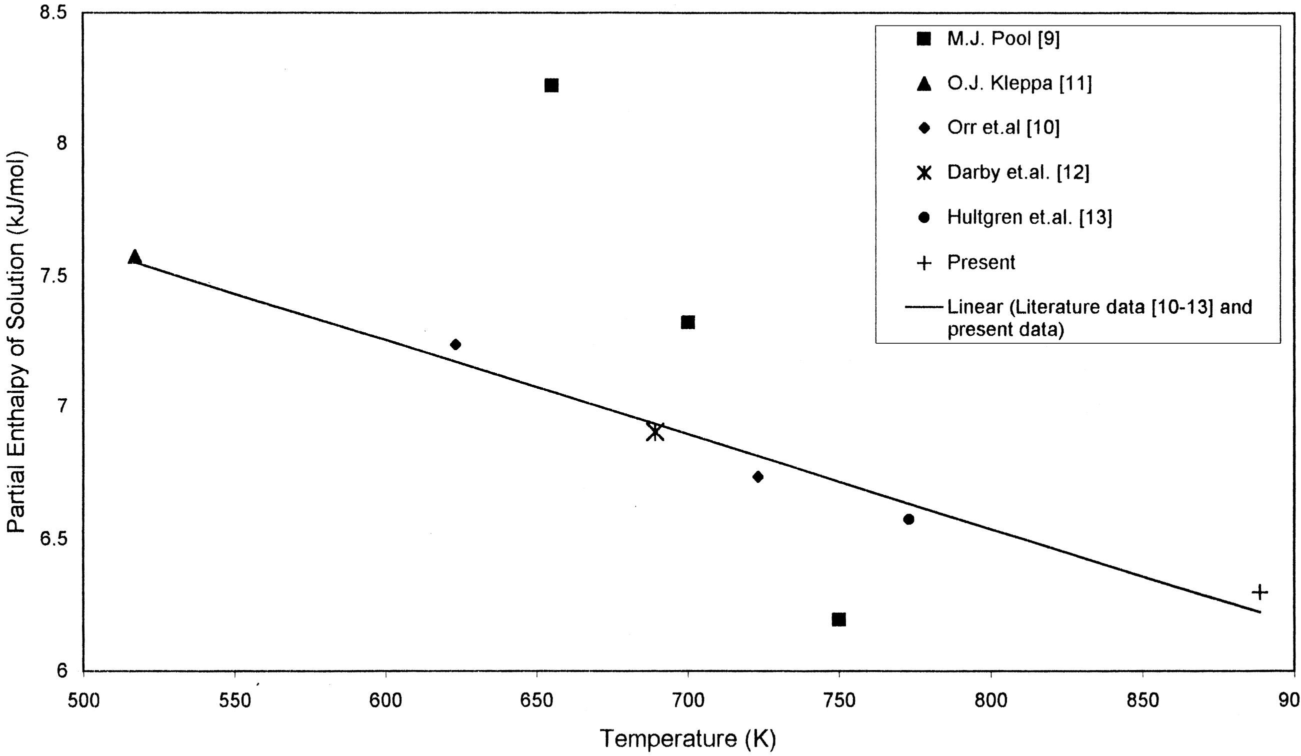

Fig. 1. Partial enthalpy of solution of cadmium in tin.

while in other set nickel was added from 1147.1 K into tin at 910 K. The partial enthalpy of solution values reported for both the set are quite similar. In present experiments, the partial enthalpy of solution of solid nickel added from 298.15 K into liquid tin at 888.75 K was found to be −41.36 kJ/mol. To be able to compare present experimental value with literature data, enthalpy of solution of liquid nickel in liquid tin at 888.75 K ($\Delta\overline{H}^{o}_{\mathrm{sol,Ni}}$) was calculated by subtracting enthalpy increment of nickel ($\Delta\overline{H}^{888.75\ \mathrm{K}}_{298.15\ \mathrm{K}}(\mathrm{Ni})$) and enthalpy of fusion of nickel metal from the present partial enthalpy of solution value (−41.36 kJ/mol). All these partial enthalpy of solution values in liquid tin are listed in Table 4. The partial enthalpy of solution values selected by Hultgren et al. [13] are less exothermic compared to present value. This could be due to an incomplete dissolution of high melting nickel metal in liquid tin. Even in the present experiments, much lower enthalpy of dissolution values were obtained when small nickel granules were used for the experiments. However, present values were obtained by adding small pieces of a very thin nickel foil that dissolved completely.

Table 4
Partial enthalpies of solution of nickel in liquid tin at infinite dilution. Ni (liq, T(K)) + Sn (liq, T(K)→Ni (Sn, T(K)) (∞ dilution)

References	Temp (K)	$\Delta\overline{H}^{o}_{\mathrm{sol,Cd}}$ (kJ/mol)
Hultgren et al. [13]	650	−71.57
	700	−68.89
	800	−63.58
	900	−58.22
Hertz [14]	623.15	−70.82
	665.65	−70.52
	743.15	−67.05
Oriani and Murphy [15]	913.15	−57.07
Day and Hultgren [16]	910.6	−58.98
Leach and Bever [17]	623.15	−63.64
Present value	888.75	−41.36–35.69 = −77.05

3.4. Enthalpies of formation of $Cd_{0.83}Ni_{0.17}$ and $Cd_{0.5}Ni_{0.5}$ compounds

The enthalpy of formation of the compounds was calculated by combining the partial enthalpies of solution of the compounds with those of the constituent elements.

$$\mathrm{Cd(298.15\ K)} \rightarrow \mathrm{Cd(Sn)(T)} \qquad \Delta H_1$$

$$\mathrm{Ni(298.15\ K)} \rightarrow \mathrm{Ni(Sn)(T)} \qquad \Delta H_2$$

$$\underline{\mathrm{Cd}_x\mathrm{Ni}_{(1-x)}\ \mathrm{(298.15\ K)} \rightarrow x\ \mathrm{Cd(Sn)\ (T)} + (1-x)\ \mathrm{Ni(Sn)\ (T)}} \qquad \Delta H_3$$

$$x\ \mathrm{Cd(298.15\ K)} + (1-x)\mathrm{Ni\ (298.15\ K)} \rightarrow \mathrm{Cd}_x\mathrm{Ni}_{(1-x)}\ \mathrm{(298.15\ K)} \qquad \Delta H^{o}$$

Where, ΔH_1, ΔH_2 and ΔH_3 are the partial enthalpies of solution of the compounds and their constituent elements, cadmium and nickel, added from 298.15 K in the tin bath at experimental temperature T(K). These are partial en-

Table 5
Partial enthalpies of solution of $Cd_{0.83}Ni_{0.17}$, $Cd_{0.5}Ni_{0.5}$, cadmium and nickel added from 298.15 K into the liquid tin at temperature 888.75 K, at infinite dilution

	$Cd_{0.83}Ni_{0.17}$	$Cd_{0.5}Ni_{0.5}$	Cd	Ni
$\Delta\overline{H}^{o}_{sol}$ (298.15 K) (kJ/mol)	25.55±0.1	12.68±0.1	29.45±0.05	−41.36±0.05

thalpies of solution at infinite dilution. Any small consecutive additions of $Cd_{0.83}Ni_{0.17}$ did not show any compositional dependence. However, partial enthalpy of solution of $Cd_{0.5}Ni_{0.5}$ showed a slight compositional dependence. It was corrected by extrapolating experimentally determined enthalpy of solution data to the composition $X_{Cd_{0.5}Ni_{0.5}} = 0.0$. The enthalpies of formation of the compounds at 298.15 K were calculated from the following equation:

$$\Delta H^{o}_{f}\,(Cd_{x}Ni_{(1-x)})\text{ at }298.15\text{ K} = x\,\Delta H_1 + (1-x)\,\Delta H_2 - \Delta H_3. \tag{6}$$

The experimentally determined partial enthalpies of solution of pure cadmium and nickel metals and the intermetallic compounds, $Cd_{0.83}Ni_{0.17}$ and $Cd_{0.5}Ni_{0.5}$, in liquid tin at infinite dilution are given in Table 5.

The enthalpies of formation of $Cd_{0.83}Ni_{0.17}$ and $Cd_{0.5}Ni_{0.5}$ intermetallic compounds at 298.15 K, calculated using Eq. (6), are −8.14 and −18.64 kJ/mol, respectively. The enthalpy of formation of $Cd_{0.83}Ni_{0.17}$ agrees well with the value −8.16 kJ/mol given by Tajbergenova et al. [18], calculated from e.m.f. data. No thermodynamic data is available in literature for $Cd_{0.5}Ni_{0.5}$ compound.

The fef and S^{0}_{T} values of $Cd_{0.83}Ni_{0.17}$ compound were calculated using ΔS^{0}_{f} (298.15 K) of the compound given by Tajbergenova et al. [18], −16.32 J/mol.K, $S^{0}_{298.15\text{ K}}$ values of cadmium and nickel given by Hultgren et al. [7], 51.80 and 29.87 J/mol.K, respectively, and the enthalpy increment data acquired in present work.

$$S^{0}_{298.15\text{ K}}(Cd_{0.83}Ni_{0.17}) = \Delta S^{0}_{f}(298.15\text{ K}) + 0.83\,S^{0}_{298.15\text{ K}}(Cd) + 0.17\,S^{0}_{298.15\text{ K}}(Ni), \tag{7}$$

$$S^{0}_{T}(Cd_{0.83}Ni_{0.17}) = S^{0}_{298.15\text{ K}}(Cd_{0.83}Ni_{0.17}) + \int_{298.15\text{ K}}^{T} \frac{C_p(Cd_{0.83}Ni_{0.17})}{T}\,dT, \tag{8}$$

$$\text{fef}(Cd_{0.83}Ni_{0.17}) = S^{0}_{T}(Cd_{0.83}Ni_{0.17}) - \frac{(H^{0}_{T} - H^{0}_{298.15\text{ K}})Cd_{0.83}Ni_{0.17}}{T}. \tag{9}$$

The thermodynamic parameters, S^{0}_{T} and fef, calculated for the compound $Cd_{0.83}Ni_{0.17}$ at various temperatures using the Eqs. (7)–(9) are listed in Table 6.

Table 6
Calculated S^{0}_{T} and fef values of $Cd_{0.83}Ni_{0.17}$ at various temperatures

T(K)	300	400	500	600	700
S^{0}_{T} (J/mol.K)	31.91	39.24	45.17	50.22	54.66
fef (J/mol.K)	31.74	32.73	34.65	36.83	39.07

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