

Determination of Thermodynamic Interaction Parameters in Solid V-Ti Alloys Using the Mass Spectrometer

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The Knudsen effusion method was combined with a mass spectrometer sensing technique in order to measure thermodynamic quantities of solid solution alloys of V-Ti binary system. The technique makes use of the regular solution model in order to treat the vaporization data in terms of ion current ratios obtained from the mass spectrometer. Within the experimental temperature range of 1500° to 1725°C and the composition range of $0.10 < N_{Ti} < 0.90$, the activity of titanium in the bcc (β) phase relative to pure titanium for the binary alloy is:

$$RT \ln a_{Ti} = RT \ln N_{Ti} + N_V^2(1.82 \pm 0.13) \text{ kcal per g-atom}$$

while the activity of vanadium is:

$$RT \ln a_V = RT \ln N_V + N_{Ti}^2(1.82 \pm 0.13) \text{ kcal per g-atom.}$$

The experimental result on the pairwise interaction parameter agrees well with the theoretically calculated value.

THERE is presently a substantial interest in the theory and properties of transition metal alloys. The investigation of the thermodynamic properties of transition metal binary systems can also yield useful information if the thermodynamic behavior can be related to observed physical properties. In addition, mass spectrometer techniques have been shown to be quite useful in several binary alloy systems studies.¹⁻³

The purpose of the present study was to investigate the utility of the time-of-flight mass spectrometer technique to relatively low vapor pressure elements in the solid solution phase and where electromotive force measurements are not readily applicable. The V-Ti system was chosen because of its complete solid solubility in the 1400° to 1625°C temperature range,⁴ possible application to alloy theory, and potential utility of some V-Ti alloys for cladding material in liquid metal, fast breeder reactors.⁵

The use of the effusion technique coupled with the mass spectrometer presents certain problems of calibration, sensitivity, and reproducibility which have been discussed by Belton and Fruehan,¹ Reese *et al.*,³ and Bidwell⁶ with respect to activity measurements. Briefly, the method of Reese *et al.*,³ where ion currents in the alloy are measured and ratioed with another ion current in the pure state, suffers because of differences in temperature reproducibility and machine constant variation. In order to circumvent this, Hoch *et al.*⁷⁻⁹

developed the triple Knudsen cell technique where isotopic ratios of an element in the alloy and in the pure state can be measured simultaneously. However, this technique decreases the ion current signal because of back diffusion, and calibration runs are frequently necessary. Belton and Fruehan^{1,2} demonstrated a technique where ion current intensity ratios can be used directly by application of the Gibbs-Duhem equation but requires a graphical integration procedure which leads to inaccuracies. The method used in the present study eliminates the integration procedure by use of the regular solution model where the overall uncertainty in the measurement is contained in the determination of the pairwise interaction parameter.

THEORY

The equations used in this study were derived by Fowler and Guggenheim¹⁰ from a statistical thermodynamic approach and revised by Hardy¹¹ to include higher order terms. The excess free energy per g-atom for a binary system is written as:

$$G^{XS} = \Omega_{12}N_1N_2 + N_1^2N_2E_{121} + N_1N_2^2E_{122} \quad [1]$$

where Ω_{12} is the pairwise interaction parameter, defined as $\Omega_{12} = Z[E_{12} - (E_{11} + E_{22})/2]$, Z = coordination number, E_{12} , E_{11} , E_{22} are the interaction energies and E_{121} and E_{122} are proportional to the interaction energy correction terms due to the influence of atom type 1 (or type 2) on a bond between atoms 1 and 2. N_i is the atom fraction.

The partial excess free energies are given by

$$\bar{G}_1^{XS} = N_2^2 \{ \Omega_{12} + E_{122} + 2(E_{121} - E_{122})N_1 \} \quad [2a]$$

and

$$\bar{G}_2^{XS} = N_1^2 \{ \Omega_{12} + E_{121} + 2(E_{122} - E_{121})N_2 \} \quad [2b]$$

In this study, subscript 1 refers to titanium and subscript 2 to vanadium. Lupis and Elliott¹² derived an

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expression for a temperature dependent interaction parameter as follows:

$$\Omega = Z\omega \left(1 - \frac{T}{\tau}\right) \quad [3]$$

where Z = coordination number, $\omega = [E_{12} - (E_{11} + E_{22})/2]$, where the interaction energies were previously defined and τ represents the temperature at which the solution becomes ideal.

Subtracting Eq. [2b] from [2a], the following equation is obtained:

$$\begin{aligned} \bar{G}_1^{xs} - \bar{G}_2^{xs} &= \Omega_{12}(N_2 - N_1) + 2N_1N_2(E_{121} - E_{122}) \\ &+ N_2^2E_{122} - N_1^2E_{121} \end{aligned} \quad [4a]$$

or replacing $N_2 = 1 - N_1$

$$\begin{aligned} \bar{G}_1^{xs} - \bar{G}_2^{xs} &= (\Omega_{12} + E_{122}) + 2N_1(E_{121} - \Omega_{12} - 2E_{122}) \\ &+ 3N_1^2(E_{122} - E_{121}) \end{aligned} \quad [4b]$$

If Eqs. [2a] and [2b] correspond to the regular system with

$$\begin{aligned} E_{121} &= E_{122} \text{ and } \Omega_{12}^* = \Omega_{12} + E_{121} = \Omega_{12} + E_{122} \\ \bar{G}_1^{xs} - \bar{G}_2^{xs} &= (\Omega_{12} + E_{121})(N_2 - N_1) = \Omega_{12}^*(N_2 - N_1) \end{aligned} \quad [5]$$

Using the definition of activity and relating the ion current in the mass spectrometer to partial pressures one obtains:²⁷

$$\begin{aligned} \Omega_{12}(N_2 - N_1) + 2N_1N_2(E_{121} - E_{122}) + N_2^2E_{122} - N_1^2E_{121} \\ = RT \ln \left[\frac{I_1 N_2}{I_2 N_1} \right] + RT \ln \left[\frac{Q_2 R_2 (E - A)_2 (IA)_2 p_2^\circ}{Q_1 R_1 (E - A)_1 (IA)_1 p_1^\circ} \right] \end{aligned} \quad [6]$$

where

I = ion current

Q = electron impact ionization cross section

R = electron multiplier response

$(E - A)$ = energy of ionizing electrons minus appearance potential

(IA) = isotope abundance

p° = absolute pressure of the element in the standard state

The left-hand side of Eq. [6] contains an expression for Ω_{12} proportional to $(N_2 - N_1)$ or $(1 - 2N_1)$ and higher-order terms which are nonlinear in N_1 . The right-hand side of Eq. [6] contains all the mass spectrometer constants and the ratio of the pressures of the elements in their standard state in addition to the term involving the ion current ratios. If as a function of composition, the ion current ratios are measured and suitably plotted, the slope yields the value of the pairwise interaction parameter Ω_{12}^* , and the intercept yields a value of the constant term by assuming $E_{121} = E_{122}$. Hence, if several temperatures are used, isothermal plots can be made to determine the temperature dependency of Ω_{12}^* . In addition, the self-consistency of the data can be determined by calculating the value of the intercept independently from equilibrium vapor pressures and by determining the relative electron impact ionization cross sections.²⁷

EXPERIMENTAL PROCEDURE

The mass spectrometer used in this study was a Bendix Model 12-107 with the five electron grid, three ion grid source modified for 20 kHz operation. The Knudsen cell inlet system and analog output system is essentially that of the commercial instrument except for modifications as noted. A detailed description of the time-of-flight mass spectrometer (TOFMS) has been reported by Wiley and McLaren¹³ and a review of the newest improvements in the instrument has been published by Damoth.¹⁴ In the mass spectrometer, neutral molecules are bombarded by a pulsed electron beam to form positive ions, which are drawn out and accelerated by -750 v and -2.8 kv accelerating grids down a 170 cm field free-drift tube. The masses are separated by the time-of-flight of ion bunches by their mass/charge ratio and are detected by an electron multiplier. An analog output circuit is used to detect and display the mass peaks on an oscilloscope or recorder. Usually, the mass spectrometer is operated at 10 kHz; however, in order to improve sensitivity, the instrument was modified for 20 kHz operation and the length of the ionizing electron beam pulse was increased from 0.25 to 0.75 μ sec. A pumping baffle was installed between the ion source and cold trap in order to increase sensitivity further. With the instrument used, vanadium signals were detected at 1400°C ($\sim 10^{-8}$ atm) with a Knudsen orifice diameter of 0.025 in. and electron energy of 18 ev. Parametric experiments performed with the TOFMS indicated that optimum ion current signals were obtained with 18 ev electron energy because of high background at higher electron energy and sensitivity.

The Knudsen assembly consisted of a tantalum outer cell with a tungsten liner which held the samples. The cell was positioned 5 to 6 cm below the ionizing region of the mass spectrometer and was adjusted horizontally to maximize the flux of particles into the ion source by maximizing the ion currents. Heating of the Knudsen cell was by electron bombardment from two-10 mil tungsten filaments. The Knudsen cell power supply (Bendix Model 925) was modified to utilize the electromotive force from a thermocouple to control emission voltage/current.²⁸ The control circuitry (Thermac Controller Model MPRY) used gate turn-off switching circuits as input control to the filament power transformers. The firing circuits control the firing time to silicon-controlled rectifiers such that these units synchronously switch the line to the filament power transformers for discrete intervals within each cycle of the line frequency. Ramp gating of the phase firing circuitry, utilizing a 300 m-sec delay, during "heat-on" and "heat-off" is used to reduce flyback action and assures asymmetrical firing of control outputs. Closed-loop current limiting is imposed to prevent thermal shock of filaments and arc-over. The controller was modified so that in case the thermocouple is shorted or damaged, the controller will shut off power and provide thermocouple protection rather than runaway heating.

The temperature of the Knudsen cell was measured by a W-5 pct Re/W-26 pct Re thermocouple which was placed in a 0.070 in. hole drilled to a depth of 0.375 in. in the bottom of the cell at a distance of 0.178 in. from center. The thermocouple replaced one of the three

tungsten rods which support the tantalum Knudsen cell and was fed into the heating tower through a vacuum connector. The thermocouple was insulated with BeO and had a 9.0 in. long, 0.062 in. diam grounded tantalum sheath. Calibration of the thermocouple was performed by visually observing melting points of various elements. Samples of Cu, Ag, Ni, Fe, Pt, Ti, and Gd were placed on either zirconia or thoria discs in the cell and were observed by a 20X telescope, sighting directly into the Knudsen cell orifice. These elements had very distinct and reproducible melting points with a maximum deviation of $\pm 5^\circ\text{C}$ in the temperature range of 950° to 1750°C .

The samples used in this study were obtained from Oak Ridge National Laboratory.⁵ These alloys were prepared by arc-melting the appropriate amounts of the pure metals at 10 wt pct increments across the entire composition range. After swaging, the specimens were then homogenized for 16 hr at 1500°C . Electron microprobe examination detected no significant inhomogeneity. Chemical analysis and other details about the sample preparation procedure are contained in a paper on self-diffusion using these alloys⁵ (see Table I for alloy compositions).

Collimated Langmuir experiments can be performed since an interesting feature of the ion current ratio method is that the usual effusion restrictions are not critical.¹⁵ Belton and Fruehan² have shown that Knudsen equilibrium conditions are not required and that a collimated Langmuir experiment will yield the same results. From rigorous kinetic theory, Evans *et al.*²⁵ have shown that in diffusive flow at all pressures, the ratio of the fluxes of the gas components is inversely proportional to the ratio of square roots of the molecular weights: the same result of Knudsen flow. Therefore, the mass spectrometer serves as a sensitive sampling device to analyze the gas mixture and the ion current ratio is correct as long as the vaporization coefficients are one, and this is usually the case for clean metal surfaces. Absolute calibration of the mass spectrometer is eliminated when using the ion current ratio method.

The surface depletion was estimated by considering a mass balance of the surface of the vaporization area, and by applying the rate equation for vaporization and by solving the unsteady state diffusion equation with the proper boundary conditions as given by Bolsaitis and Skolnick.¹⁶ The solution of the diffusion equation is¹⁷

$$\frac{X^s}{X_0} = \exp(\alpha^2) \operatorname{erfc}(\alpha) \quad [7]$$

Table I. Chemical Analysis of Ti-V Alloys

Nominal Composition	Wt Pct V	Wt Pct Ti	Wt Pct C	Wt Pct O ₂	Wt Pct N ₂
10 V-90 Ti	10.0	89.4	0.041	0.28	0.022
20 V-80 Ti	20.2	80.4	0.010	0.092	0.0081
30 V-70 Ti	30.6	69.8	0.039	0.29	0.027
40 V-60 Ti	40.3	59.1	0.035	0.24	0.024
50 V-50 Ti	50.5	50.1	0.029	0.21	0.038
60 V-40 Ti	60.0	40.2	0.037	0.12	0.048
70 V-30 Ti	70.5	30.1	0.032	0.040	0.046
80 V-20 Ti	80.0	20.7	0.060	0.040	0.075
90 V-10 Ti	90.2	9.88	0.049	0.089	0.089

where

$$\alpha = 5.83 \times 10^{-2} \frac{kA_0\gamma t^{1/2} P_0}{A\rho(MT)^{1/2} D^{1/2}} = B \frac{t^{1/2} P_0}{D^{1/2}} \quad [7a]$$

and

$$B = 5.83 \times 10^{-2} \frac{kA_0\gamma}{A\rho(MT)^{1/2}} \quad [7b]$$

B varies slowly with temperature, whereas P_0 and D vary exponentially,

where

X^s/X_0 = ratio of surface to bulk concentration

k = clausung factor of orifice ($\approx \frac{1}{2}$)

γ = activity coefficient (≈ 1)

A_0/A = ratio of orifice to sample surface area

P_0 = vapor pressure of effusing component at temperature, torr

D = diffusion coefficient, $\text{cm}^2 \text{sec}^{-1}$

ρ = molar density, g per mole

M = at. wt, g ~ 50

t = time, sec

T = absolute temperature, $^\circ\text{K}$ ($\sim 2000^\circ\text{K}$)

For $D \approx 10^{-8}$ sq cm per sec, and making approximations for the other quantities, the ratio of surface to bulk concentration was calculated, using Eq. [7], to be a maximum of 5 pct with orifice-to-surface area ratios of less than 0.01 and time of 3 min. Since the use of Eq. [7] is based on approximations, surface depletion effects are best tested by experimental results. Usually, the maximum errors for surface depletion effects are less than the overall accuracy of the data since no measurable change in ion current was detected for sample surface-to-orifice area ratios > 100 . Values of $D \approx 10^{-8}$ sq cm per sec have been reported by Murdock and McHargue⁵ for vanadium in Ti-V binary alloys and for titanium in Ti-V binary alloys in the temperature range of 1600°C . If values of $D \approx 10^{-11}$ sq cm per sec or three orders of magnitude less than those observed at the experimental temperature are used in Eq. [7], then errors arising from surface depletion can become significant.

The weight loss of a sample during an experimental run was usually about 0.3 wt pct so that no noticeable composition change was taking place in the alloy during the experiment, since both species were monitored and detected.

Before any experimental data with alloys were obtained, the tantalum Knudsen cell and tungsten liners were chemically cleaned or cleaned by heating in the Knudsen tower or in a separate vacuum furnace. Chemical cleaning was done in a 4:1 solution of $\text{HNO}_3:\text{HF}$ for several minutes. The advantage of chemically cleaning was that it was fast, taking a few minutes, whereas heating in the Knudsen tower usually takes about 2 hr. Heating in the Knudsen tower accomplished another purpose because the cell was degassed and the background signals could be determined.

After chemically cleaning the crucible and liner, the Knudsen cell was placed in the heating tower of the TOFMS where it was heated to between 50° and 100°C

higher than the experimental temperature, and background signals for nominal mass numbers of 48, 51 were determined. This was done by aligning the Knudsen cell and recording a shutter open and shutter closed ratio. When there was no detectable change, the signal was background. If the signal was on the 0.01 electrometer scale, the cell was purposely misaligned and a shutter open to shutter closed ratio was determined again. If the signal showed no change, the Knudsen cell was removed and an alloy sample was placed in the tungsten liner for a vaporization experiment.

Prior to loading the alloy sample, which was usually in the form of $\frac{3}{8}$ by $\frac{1}{16}$ by $\frac{3}{16}$ in. slugs, into the heating tower, the samples were chemically cleaned with a 4:1 ratio of HNO_3 :HF solution for approximately 30 sec. The samples were then placed in the tungsten liner which was placed in the tantalum Knudsen cell and loaded into the TOFMS inlet chamber. The alloy sample was heated to 1000°C slowly to allow for degassing and remained at that temperature until a vacuum of 10^{-5} torr was maintained. The temperature was then increased slowly in smaller increments so that the vacuum remained near 5×10^{-5} torr. When the sample temperature reached 1500°C, a 40 liter per sec ion pump was used to augment vacuum pumping so that a vacuum of 10^{-5} torr or more was maintained during the experiment.

While heating, degassing, background determination, and so forth, were being done, the electrometers were zero-balanced prior to each experimental run. When two or more electrometers were used, they were balanced against a secondary calibrated argon leak¹⁸ signal by changing the gate width. By reproducing the same argon signal on two or more electrometers, they were balanced with respect to each other and thus would produce ion current ratios directly. Argon signals were recorded at the beginning, during, and at the conclusion of the experiment to verify the balance. Thus, even if the absolute value of the argon signal varied, the electrometer balance could be maintained and ion current ratios would be constant.

At 1500°C, ion current signals were recorded. The temperatures were changed at random from 1500° to 1700°C, depending on the alloy, in 50°C temperature increments up to 50°C below the melting point of the alloy. At least one temperature was repeated to determine the reproducibility of the ion current signals. At each temperature, the shutter open and shutter closed ratio was determined and a compensation for background was made, if necessary. Initially, the ion current species was scanned at least 10 times at each temperature. However, by using two electrometers set on each of the ion current signals, it was possible to take continuous measurements so that the ion current ratio could be obtained directly.

During the experimental run, alignment was checked visually and the crucible position was varied to maintain maximum ion current signals. Titanium isotope ratios were determined to check the scale factors for the electrometers and overall operation of the TOFMS. 10 min were allowed between temperature excursions; however, it was determined that Knudsen cell equilibration took place 3 min after changing the power level. Continuous ion current signals were taken for about 10 min after temperature equilibrium was attained. Shutter open and shutter closed ion current data were taken for

similar periods of time, although background signals did not change very much during an experimental run and was usually on the 0.01 electrometer scale.

RESULTS AND DISCUSSION

The ion current ratios associated with nine alloys over the temperature range of the experiments were obtained. A least square fit was made to the data using an IBM 7094 computer for a plot of $RT \ln [(\Delta I_{48}^+/\Delta I_{51}^+) \times (N_2/N_1)]$ vs $(N_2 - N_1)$ to obtain a straight line. The term ΔI^+ refers to the difference in ion current intensity above background signal at the nominal mass number. The data were systematically reviewed for large standard deviations from the average ion current ratios, and for signal-to-background ratios of less than 10. The ion current ratio data were analyzed in two ways, first with signal-to-background ratios >10 and second, using all data regardless of signal-to-background ratio.

Using the theoretical analysis expressed in Eq. [6] and assuming $E_{121} = E_{122}$ as a first approximation, all data points were best fitted to a straight line shown in Fig. 1. The standard deviation of the straight line was determined by statistical methods,¹⁹ assuming error in Y-axis. The standard deviation in the slope is given by¹⁹

$$s_b = s_y \sqrt{\frac{k}{k \sum x_n^2 - (\sum x_n)^2}}$$

where

$$s_y = \sqrt{\frac{\sum (\delta y_n)^2}{k - 2}}$$

and

$$\sum (\delta y_n)^2 = \sum y_n^2 - \frac{(\sum y_n)^2 \sum x_n^2 - 2 \sum (x_n y_n) \sum x_n \sum y_n + k [\sum (x_n y_n)]^2}{k \sum x_n^2 - (\sum x_n)^2}$$

The standard deviation in the intercept is

$$s_a = s_y \sqrt{\frac{\sum x_n^2}{k \sum x_n^2 - (\sum x_n)^2}}$$

where the terms are defined previously and k is the number of data points used.

The data plotted in Fig. 1 are easily fitted to a straight line indicating that the assumption $E_{121} = E_{122}$

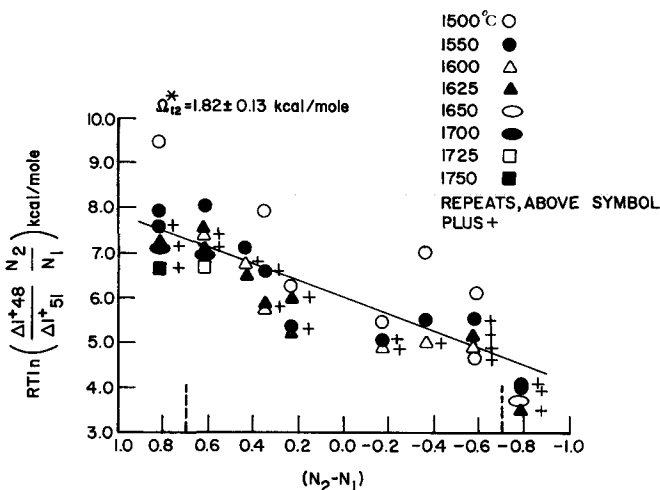


Fig. 1—Plot of $RT \ln [(\Delta I_{48}^+/\Delta I_{51}^+) \cdot (N_2/N_1)]$ vs $(N_2 - N_1)$ for binary alloy V-Ti.

is justified. When consideration is made for data points obtained with signal-to-background ratios of <10, the data show that the experimental error is random, *i.e.*, there is no systematic error in the experiment. The solid line in Fig. 1 has been fitted using all data (78 points) including those data with signal-to-background ratios <10. A similar line can be obtained using data with signal-to-background ratios >10 only (37 points) with the same results, within experimental error. The slope of the solid line (best fit of data) in Fig. 1, is the pairwise interaction parameter, *i.e.*, 1.82 ± 0.13 kcal per g-atom.

Isothermal plots of $RT \ln [(\Delta I_{48}^*/\Delta I_{51}^*) \cdot (N_2/N_1)]$ vs $(N_2 - N_1)$ were made at several experimental temperatures using the same criteria of signal-to-background ratio >10. Although the best fit of these data to straight lines was about the same, at lower temperatures the experimental scatter was higher. These results are tabulated in Table II and indicate no noticeable temperature dependency of the pairwise interaction parameter. Consistency of the data can be determined from the constancy of the intercept, which can be calculated independently, since values for the individual terms which comprise the constant term of Eq. [6] are known. The method used in this investigation was to calculate values for relative electron impact ionization cross sections and compare them to theoretically calculated values of Ötvös and Stevenson²¹ and Mann.²² The agreement was surprisingly good.²⁷

Since vanadium is a β -stabilizing element for titanium, theory⁹ predicts a positive value for the pairwise interaction parameter. The positive interaction parameter indicates positive deviation from ideal behavior and clustering of like atoms in the β phase of Ti-V alloys. The Ti-V binary phase diagram does not exhibit a miscibility gap,⁴ and the lowest temperature where the phase diagram has been studied is 800°K. Ω^* must be less than $2RT_c$ (Ref. 26) or $2R(800) = 3.2$ kcal per g-atom.

Hoch²⁴ calculated the difference in Ω_{12}^* between liquid and bcc Ti-V alloys from the phase diagram and found $\Omega_{12}^{*\beta} - \Omega_{12}^{*\alpha} = 1.3$ kcal per g-atom. It should be noted

that Ω_{12} assumes $E_{121} = E_{122} = 0$ and Ω_{12}^* assumes $E_{121} = E_{122} \neq 0$. As Hoch *et al.*⁹ have pointed out previously, $\Omega_{12}^{*\alpha}$ and $\Omega_{12}^{*\beta}$ should be both positive or negative, and $\Omega_{12}^{*\beta}$ larger in absolute value than $\Omega_{12}^{*\alpha}$. Thus, in this case, $\Omega_{12}^{*\beta} > \Omega_{12}^{*\alpha} > 0$, and $\Omega_{12}^* > 1.3$ kcal per g-atom. Thus from the phase diagram $1.3 < \Omega_{12}^* < 3.2$ kcal per g-atom or about $\Omega_{12}^* = 2.2 \pm 1.0$ kcal per g-atom. The experimental value of 1.82 ± 0.13 kcal per g-atom is in excellent agreement with this estimate, and also in good agreement with the theoretical calculation of Kaufman and Bernstein²⁰ who calculated a value of 2.66 kcal per g-atom.

Van Ostenburg *et al.*²³ measured Knight shifts of V^{51} in the Ti-V binary system. In order to explain their results and the high resistivity in transition metals in general, they adopted the viewpoint that the conduction electron wave function is composed of an admixture of *s*- and *d*-states with the electrons resonating between them. The *s*- and *d*-resonance concept implies that the $3d$ levels cannot be transferred and would give a positive deviation from ideal behavior and thus, a positive value for the pairwise interaction parameter.

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Table II. Interaction Parameters from Experimental Data on Ti-V Alloys

Temp Range, °C	Slope (Ω_{12}^*), kcal per g-atom	Intercept, kcal	Number of Points	Comment
1550° to 1725°C	1.95 ± 0.11	5.78 ± 0.06	37	Signal background ratio >10, 18 ev
1500° to 1725°C	1.87 ± 0.12	5.68 ± 0.06	43	Signal background ratio >10, 15 to 18 ev
1500° to 1725°C	1.82 ± 0.13	5.94 ± 0.07	78	All points
1625°C	2.48 ± 0.21	5.43 ± 0.12	12	Signal background ratio >10
1600°C	1.65 ± 0.21	5.73 ± 0.10	19	Signal background ratio >10
1600°C	1.62 ± 0.18	5.83 ± 0.09	24	All points
1550°C	0.63 ± 0.35	5.53 ± 0.12	6	Signal background ratio >10
1550°C	1.95 ± 0.22	6.02 ± 0.11	23	All points
1500°C	2.48 ± 0.54	6.73 ± 0.28	12	Signal background ratio >10

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